CHEMCOMM
Communication
www.rsc.org/chemcomm

A new binuclear ruthenium complex with an annelated C_7 bridge *via* an unprecedented [2 + 2] coupling reaction†

Stéphane Rigaut,*[a] Luc Le Pichon,[a] Jean-Claude Daran,[b] Daniel Touchard*[a] and Pierre H. Dixneuf[a]

[a] *Institut de Chimie de Rennes, UMR 6509 CNRS-Université de Rennes: Organométalliques et Catalyse, Campus de Beaulieu 35042 Rennes, France. E-mail: daniel.touchard@univ-rennes1.fr*
[b] *Laboratoire de Chimie de Coordination, 205 Route de Narbonne, 31042 Toulouse Cedex, France*

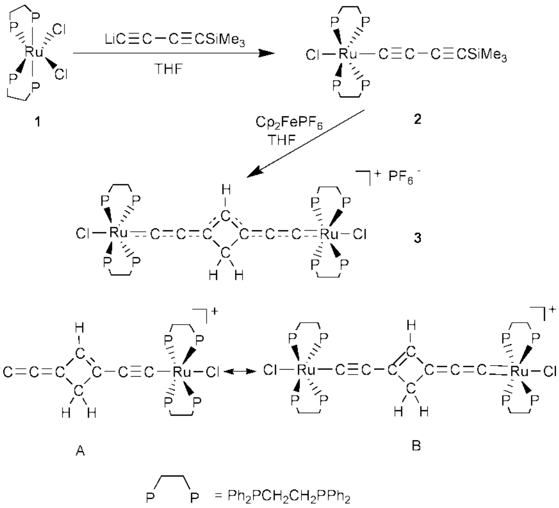
Received (in Cambridge, UK) 12th April 2001, Accepted 22nd May 2001
First published as an Advance Article on the web 14th June 2001

Treatment of $[Cl(dppe)_2Ru–C{\equiv}C–C{\equiv}C–SiMe_3]$ with $[Fe(C_5H_5)_2]PF_6$ leads to an unprecedented metal-assisted [2 + 2] coupling reaction on $C^{\gamma}{\equiv}C^{\delta}$ bonds to obtain $[Cl(dppe)_2Ru–C{\equiv}C–C{=}CHC(CH_2){=}C{=}C{=}Ru(dppe)_2Cl]PF_6$ with the charge highly delocalized over seven carbon atoms and including a cyclobutenyl bridge; the crystal structure was solved.

Polynuclear transition metal complexes with unsaturated carbon rich bridges retain much attention,[1,2] for their potential to scale down electronic components *i.e.* to form molecular wires and other nanoelectronic devices.[2] The literature is now extensive for complexes with an even number of conjugated carbon atoms spanning two metal fragments of various structures[1,2] such as $L_nMC_xML_n$ or $L_nM(CH)_xML_n$. By contrast, the synthesis of bimetallic compounds with odd carbon chains has not been extensively explored considering the variety of fragments available. Only few bridges with one, three or five unsaturated carbons capped with two metal moieties have been reported.[3–5] Current extension of the chemistry of vinylidene $[M{=}C{=}CR^1R^2]$ and acetylide $[M–C{\equiv}C–R]$ complexes to obtain new bridges *via* [2 + 2] cycloaddition led to a class of complexes $[M–C{=}CR–C(CR^2R^3){=}M]^+$ including rigid cyclic four-membered bridges with a delocalised C_3 path between metals.[4,5] Interestingly, when the reaction was applied to allenylidene[4c] $[M{=}C{=}C{=}CR^1R^2]$ or diyne[4d] $[M–C{\equiv}C–C{\equiv}C–R]$ complexes, the resulting ring bears an exocyclic double or triple bond, respectively, with a similar C_3 conjugated path. The formation of these carbon ligands is highly regioselective and the product of addition with the most activated $C^{\alpha}–C^{\beta}$ bond is always obtained. We now report an unprecedented radical-promoted [2 + 2] coupling reaction occurring on the $C^{\gamma}{\equiv}C^{\delta}$ bonds of a 1,3-diynyl metal derivative to lead to a novel type of metal complex $[M–C{\equiv}C–C{=}CHC(CH_2){=}C{=}CM]^+$ including a carbon-rich annelated C_8H_3 bridge with seven conjugated carbons between remote metals.

Previous studies[6] on ruthenium allenylidenes $[Cl(dppe)_2$-$Ru{=}C{=}CR^1R^2]$ and acetylides $[Cl(dppe)_2Ru–C{\equiv}C–R]$ (dppe = 1,2-diphenylphosphinoethane) showed that the bulky ruthenium $[RuCl(dppe)_2]^+$ moiety prevents C^{α} from nucleophilic attack while promoting reactions on C^{γ}. The $C^{\alpha}{\equiv}C^{\beta}$ bond in diyne complexes such as $[Cl(dppe)_2Ru–C{\equiv}C–C{\equiv}C–SiMe_3]$ is sterically protected by the dppe groups and [2 + 2] cycloaddition using this type of complex is likely to occur on the $C^{\gamma}{\equiv}C^{\delta}$ triple bond. The pale yellow diynyl ruthenium complex *trans*-$[Cl(dppe)_2Ru–C{\equiv}C–C{\equiv}C–SiMe_3]$ **2** was obtained (63%) *via* substitution of one chloride of *cis*-$[RuCl_2(dppe)_2]$ **1** with a slight excess (1.5 equiv.) of lithium acetylide in THF (Scheme 1). The *trans* structure was evidenced by ^{31}P NMR spectroscopy showing a singlet at δ 49.09 for the four phosphorus atoms. Upon treatment of complex **2** with half an equivalent of ferrocenium hexafluorophosphate as oxidant a metal-assisted C–C forming reaction took place and dark purple crystals of **3** were isolated after several crystallisations in moderate yield (45%). This compound was fully characterised by NMR, IR, UV–VIS and HR-MS (ESI†). ^{31}P analysis of **3** shows only one singlet at δ 45.2 indicating that (i) the two metal sites are equivalent and (ii) the four phosphorus are also equivalent on each metal centre with the Cl atom and the bridge in a *trans* position. ^{13}C NMR analysis shows only five different signals for the unsaturated bridges linking the two rutheniums. The Ru–C(1) resonance at δ 247.7 (quint, $^2J_{pc}$ 14 Hz) is downfield compared to that of an alkynyl (δ 105.5 for $[Cl(dppe)_2Ru–C{\equiv}C–CPh_2H]$)[6b] and upfield from that of an allenylidene complex (δ 308.6 for $[Cl(dppe)_2Ru{=}C{=}C{=}CPh_2]$).[6c] The same phenomenon is observed for the C(2) (δ 166.0) and C(3) (δ 147.1) resonances. The ^1H spectrum shows two characteristic resonances for the C_4 ring at δ 2.07 (s, 2H) and δ 5.11 (s, 1H). These NMR studies are consistent with a highly delocalized structure giving a formal half positive charge on each ruthenium as sketched on Scheme 1. The FTIR spectrum shows an intense absorption band at 1909 cm^{-1} indicative of the cumulenylidene character of the system.[6a,c]

X-Ray-structural analysis[7] (Fig. 1) verifies that the complex is formed with two identical bulky ruthenium fragments $[RuCl(dppe)_2]^+$ connected by a C_8H_3 ligand. The Cl atoms adopt a *trans* position with respect to the bridge and the Cl(1)–Ru(1)–bridge–Ru′(1)–Cl(1)′ arrangement is linear. The four-membered ring is planar so giving maximum orbital overlap across the bridge. Owing to the inversion centre which relates the two parts of the complex, the four-membered ring is symmetric. Moreover as the two distances, C(3)–C(4) 1.457(5) Å and C(3)–C(4′) 1.459(5) Å, are identical within experimental error, the four C–C bond lengths are identical within the ring.[7b]



Scheme 1

---

† Electronic supplementary material (ESI) available: selected spectroscopic data. See http://www.rsc.org/suppdata/cc/b1/b103301h/

DOI: 10.1039/b103301h

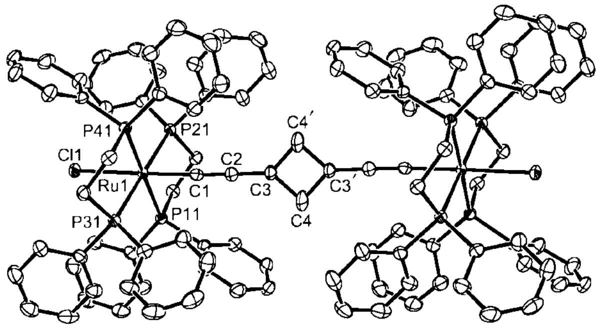


Fig. 1 Molecular structure of **3** (ORTEP view). Ellipsoids represent 50% probability level. Selected distances (Å) and angles (°): Ru(1)–C(1) 1.933(3), C(1)–C(2) 1.225(4), C(2)–C(3) 1.372(4), C(3)–C(4) 1.457(5), C(3)–C(4′) 1.459(5); C(1)–Ru(1)–Cl(1) 178.49(9), C(2)–C(1)–Ru(1) 174.4(2), C(1)–C(2)–C(3) 178.3(3), C(2)–C(3)–C(4) 134.2(3), C(3)–C(4)–C(3′) 88.3(3).

In order to account for the inversion centre, we should consider the occurrence of a fully delocalised system with a disorder between CH and CH_2. Indeed, Ru–C(1) (1.933 Å), C(2)–C(3) (1.372 Å) bonds are found to be shorter than the single bonds in an acetylenic system such as $[Cl(dppe)_2Ru–C{\equiv}C–C_6H_4NO_2)]$[8] (1.986 and 1.442 Å) and longer than the double bonds in an allenylidene system $[Cl(dppm)_2Ru{=}C{=}C{=}C(C_{14}H_{10})]PF_6$[6d] (1.852 and 1.393 Å). On the other hand the C(1)–C(2) bond length (1.225 Å) is intermediate between the values found in these mononuclear systems (1.206 and 1.255 Å, respectively) demonstrating a bond order between one and two for Ru(1)–C(1), C(1)–C(2), C(2)–C(3) bonds indicative of a hybrid structure.

The UV–VIS spectrum of the complex recorded in CH_2Cl_2 exhibits a strong charge transfer band (λ_{max} = 633 nm) with a high absorption coefficient (ε = 141 000 mol^{-1} L cm^{-1}) (ESI†). For comparison, the allenylidene compound $[ClRu(dppe)_2({=}C{=}C{=}CPh_2)]PF_6$ shows a MLCT band at λ_{max} = 505 nm, ε = 18 000 mol^{-1} L cm^{-1}. The charge transfer is considerably more intense in the bimetallic compound and this can be best rationalized by the two canonical forms A and B. It is of note that **3** shows a stronger absorption than the related 'V' shaped compound $[CpRu(PPh_3)_2{=}C{=}C{=}CH–C{\equiv}C–Ru(PPh_3)_2Cp]BF_4$ (λ_{max} = 600 nm, ε = 72 000 mol^{-1} L cm^{-1}) which exhibits the same type of conjugation between the two remote metals.[3d,9] This is certainly due to the better planarity and rigidity of **3** and subsequent stronger conjugation. Cyclic voltammetry (CV) was used to investigate the electrochemical behaviour of **3** (CH_2Cl_2, $Bu^n{}_4NPF_6$ 0.1 M 200 mV s^{-1}). The binuclear compound undergoes a well defined one-electron reversible oxidation ($E°$ = 0.42 V *vs.* ferrocene) and an irreversible second oxidation at higher potential (E_{pa} = 0.91 *vs.* ferrocene). It also shows a one-electron reversible reduction ($E°$ = −1.48 V *vs.* ferrocene). The oxidation processes can be attributed to the successive oxidation of the two ruthenium centres[3d,6c,e] due to substantial electronic interaction between the metallic centres.[2] The reduction process can be attributed to the reduction of the C_8H_3 ligand.[3e,6b,e] Indeed, carrying out the reduction of complex **3** with cobaltocene[10] in a THF solution in a capped EPR tube allows the direct observation of the radical species $\mathbf{3}^{\cdot}$ which generates an intense and persistent feature at 293 K. A signal without detectable hyperfine structure is located in a characteristic region for organic radicals with g = 2.009. The electrochemical behaviour of **3** is in accord with that found for the related 'V' shaped compound $[CpRu(PPh_3)_2{=}C{=}C{=}CH–C{\equiv}C–Ru(PPh_3)_2Cp]BF_4$.[3d]

In summary, we have developed an easy method to prepare a bimetallic complex containing a novel C_8H_3 bridge with new interesting spectroscopic and structural properties. The unprecedented regioselectivity of the addition is explained by the steric hindrance of the bulky diphosphines with only the $C^{\gamma}{\equiv}C^{\delta}$ bond being reactive.[6] Despite the unfavourable potential, the reaction is likely initiated by an electron transfer between ferrocenium and **2** ($E°$ = 0.130 V *vs.* ferrocene) generating an electrophilic organometallic radical. The latter would be able to couple with another molecule of acetylide **2**. This mechanism (and the driving force) remains unverified but we anticipate that the resulting radical incorporates hydrogen atoms from the medium.[11]

We thank the CNRS and the Université de Rennes 1 for support, Drs P. Guenot and O. Maury for helpful discussion and M. Krueger (Erasmus student) for help.

Notes and references

1 For examples, see: R. Dembinski, T. Bartik, B. Bartik, M. Jaeger and J. A. Gladysz, *J. Am. Chem. Soc.*, 2000, **122**, 810; J. Gil-Rubio, M. Laubender and H. Werner, *Organometallics*, 2000, **19**, 1365; C. Hartbaum, Z. Mauz, G. Roth, K. Weissenbach and H. Fischer, *Organometallics*, 1999, **18**, 2619; K. T. Wong, J.-M. Lehn, S.-M. Peng and G.-H. Lee, *Chem. Commun.*, 2000, 2259.

2 F. Paul and C. Lapinte, *Coord. Chem. Rev.*, 1998, **178–180**, 431; B. Hong and J. V. Ortega, *Angew. Chem., Int. Ed.*, 1998, **37**, 15; A. M. McDonagh, M. G. Humphrey, M. Samoc, B. Luther-Davies, S. Houbrechts, T. Wada, H. Sasabe and A. Persoons, *J. Am. Chem. Soc.*, 1999, **121**, 1405.

3 (*a*) T. Bartik, W. Weng, J. A. Ramsden, S. Szafert, S. B. Falloon, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1998, **120**, 11 071; (*b*) R. Dembinski, S. Szafert, P. Haquette, T. Lis and J. A. Gladysz, *Organometallics*, 1996, **18**, 5438; (*c*) G. Jia, H. P. Xia, W. F. Wu and W. S. Ng, *Organometallics*, 1997, **16**, 1; (*d*) H. P. Xia, W. S. Ng, J. S. Ye, X. Y. Li, W. T. Wong, Z. Lin, C. Yang and G. Jia, *Organometallics*, 1999, **18**, 4552.

4 (*a*) T. Bartik, M. T. Johnson, A. M. Arif and J. A. Gladysz, *Organometallics*, 1995, **14**, 889; (*b*) H. Fischer, F. Leroux, G. Roth and R. Stumpf, *Organometallics*, 1996, **15**, 13 723; (*c*) H. Fischer, F. Leroux, R. Stumpf and G. Roth, *Chem. Ber.*, 1996, **129**, 1475; (*d*) F. Leroux, R. Stumph and H. Fischer, *Eur. J. Inorg. Chem.*, 1998, 1225.

5 N. E. Kolobova, T. V. Ozantseva, Y. T. Struchkov, A. S. Batsanoy and V. I. Bakhmutov, *J. Organomet. Chem.*, 1985, **292**, 247; N. Y. Kolokova, V. V. Skripkin, G. G. Alexandrov and Y. T. Struchkov, *J. Organomet. Chem.*, 1979, **169**, 293; W. Weng; J. R. Berenguer, J. Fornies, E. Lalind, F. Martinez, L. Sanchez and B. Serrano, *Organometallics*, 1998, **17**, 1640; R. M. Bullock, *J. Am. Chem. Soc.*, 1987, **109**, 8087.

6 (*a*) D. Touchard and P. H. Dixneuf, *Coord. Chem. Rev.*, 1998, **178–180**, 409; (*b*) S. Rigaut, O. Maury, D. Touchard and P. H. Dixneuf, *Chem. Commun.*, 2001, 373; (*c*) D. Touchard, P. Haquette, A. Daridor, A. Romero and P. H. Dixneuf, *Organometallics*, 1998, **17**, 3844; (*d*) N. Pirio, D. Touchard and P. H. Dixneuf, *Chem. Commun.*, 1991, 980; (*e*) R. F. Winter, *Eur. J. Inorg. Chem.*, 1999, 2121.

7 (*a*) *Crystal data* for **3**: $C_{112}H_{99}Cl_2F_6P_9Ru_2$, M = 2110.68, triclinic, space group $P\bar{1}$, a = 9.7811(10), b = 12.1069(14), c = 20.503(2) Å, α = 95.204(13), β = 98.910(12), γ = 101.264(13)°, U = 2334.0(4) $Å^3$, Z = 1, D_c = 1.500 Mg m^{-3}, Mo-Kα (λ = 0.71073), μ = 0.599 mm^{-1}, $F(000)$ = 1079, Stoe IPDS diffractometer, T = 180(2) K, crystal size 0.24 × 0.16 × 0.08 mm, θ_{max} 24.20°, data/restraints/parameters ratio 6976/336/592, R = 0.0303, wR_2 = 0.0723 [5466 reflections with $F > 4\sigma(F_0)$], wR_2 = 0.0766 (all data), S = 0.958. CCDC 162902. See http://www.rsc.org/suppdata/cc/b1/b103301h/ for crystallographic data in CIF or other electronic format. (*b*) No H atoms could be located in the vicinity of C(4) which presents a thermal ellipsoid elongated perpendicular to the ring plane. Attempts to define a disorder model showing the possible occurrence of a C=C bond in the cycle failed.

8 M. Younus, N. J. Long, P. R. Raithby, J. Lewis, N. A. Page, A. J. P. White, D. J. Williams, M. C. B. Colbert, A. J. Hodge, M. S. Khan and D. G. Parker, *J. Organomet. Chem.*, 1999, **578**, 198.

9 The absorptions of the respective mononuclear allenylidenes present similar values of ε, see M. Tamm, T. Jentzsch and W. Werncke, *Organometallics*, 1997, **16**, 1424.

10 The potential of **3** is 150 mV negative to that of $[CoCp_2]$ (−1.33 V *vs.* ferrocene). However, the values are close enough to observe a slight displacement of the equilibrium and to detect the reduced species $\mathbf{3}^{\cdot}$ using EPR spectroscopy. See N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877.

11 It is likely that **2** is oxidized and further desilylation would lead to a radical species of type $Ru^{\cdot+}–C{\equiv}C–C{\equiv}CH \leftrightarrow Ru^{+}{=}C{=}C{=}C{=}CH^{\cdot}$ that can react with **2** [0.5 equiv. of oxidant is necessary, [2 + 2] coupling reaction]. The resulting cyclic radical would be desilylated and incorporate hydrogen atoms from the medium. It is of note that treatment of **2** with $CuCl_2$ or $FeCl_3$ also leads to **3** and that protonation of **2** with an acid (HBF_4) does not lead to **3** *via* a butatrienylidene intermediate.