Bis-allenylidene Metal Complex and Unique Related Radical with Delocalization of One Electron over Both Trans Carbon-Rich Chains

Stéphane Rigaut,*,† Karine Costuas,‡ Daniel Touchard,*,† Jean-Yves Saillard,‡ Stéphane Golhen,‡ and Pierre H. Dixneuf†

UMR 6509 CNRS-Université de Rennes 1, Organométalliques et Catalyse, and UMR 6511 CNRS-Université de Rennes 1, Laboratoire de Chimie du Solide et Inorganique Moléculaire, Institut de Chimie de Rennes, Campus de Beaulieu, 35042 Rennes Cedex, France

Received January 21, 2004; E-mail: daniel.touchard@univ-rennes1.fr; stephane.rigaut@univ-rennes1.fr

Organometallic complexes with π-conjugated bridges have gained importance for their applications in the emerging field of molecular-scale electronic devices.[1] Carbon-rich trans ditopic structures, metalla-oligomeric wires[2] constitute an interesting alternative to simple metal-capped carbon chains[3] in order to allow length control and connectivity to other components. However, bis-(alkynyl) metal complexes have been found to be mostly insulators. Indeed Pt, Pd, Hg, or Cu disrupt the π-conjugation between two acetylide chains.[4] By contrast, *trans*-bis(alkynyl) ruthenium systems increase communication between two ferrocene units in an oxidation process.[5] As the reduction of a metallacumulene $[Ru]^+=C=C=CR_2$ occurs on the carbon chain,[6] it thus appears that an original solution to create electronic communication between two carbon-rich chains connected via a metal may arise from the reduction of a bis(allenylidene) metal moiety $R_2C=C=C=[Ru]^{2+}=C=C=CR_2$ leading to single-electron delocalization. Interestingly, this kind of arrangement has never been achieved despite the fascination displayed by its structure and its attractive potential as a key connecting group in the field of nanoscaled molecular wires. We now report the preparation of the first real bis(allenylidene) metal complex[7] and especially the evidence that the reduced species leads to a novel symmetric radical that has one unpaired electron delocalized over both trans carbon-rich chains, a phenomenon supported by computational studies.

An attempt to produce the target moieties *trans*-$[Ph_2C=C=C=(dppe)_2Ru=C=C=CPh_2]^{2+}$ (3^{2+}) from *trans*-$[Cl(dppe)_2Ru=C=C=CPh_2]PF_6$ (**A**) (dppe = 1,2-diphenyl-phosphinoethane) using the Selegue method[8] failed, as the halide is not labile. An alternative method is based on the two-electron oxidation and deprotonation of $[Ru]^+-C≡C-CHPh_2$ group.[6b] Thus, the allenylidene-acetylide *trans*-$[Ph_2C=C=C=(dppe)_2Ru-C≡C-CHPh_2]PF_6$ ($2^+PF_6^-$) was first prepared from **1** and submitted to oxidation reaction according to Scheme 1. Complex $2^+PF_6^-$ ($E° = 0.82$ V vs ferrocene) was reacted overnight with an excess of Ce^{IV} ammonium nitrate in CH_2Cl_2. The oxidation reaction leads to the elimination of the γ proton, and to the bis(allenylidene) complex $3^{2+}[B(C_6F_5)_4^-]_2$ (80%) as a blue solid that has been fully characterized. The FTIR spectrum presents an intense absorption at 1923 cm^{-1}, characteristic of the allenylidene substituents. The ^{31}P NMR analysis shows one singlet at 42.3 ppm, typical for a symmetrical structure, indicating the trans disposition of the chains. The ^{13}C NMR spectrum displays only three different signals for the cumulenic carbon atoms. The C_α carbon atom resonance at very low field with respect to the bis-(alkynyl) complex[7] is consistent with allenylidene species ($\delta = 297.6$ ppm), close to that of **A** ($\delta = 308.5$ ppm). The UV−visible spectra, recorded from the deep blue solution of $3^{2+}[B(C_6F_5)_4^-]_2$

Scheme 1. Synthesis and Reactivity of 3^{2+}
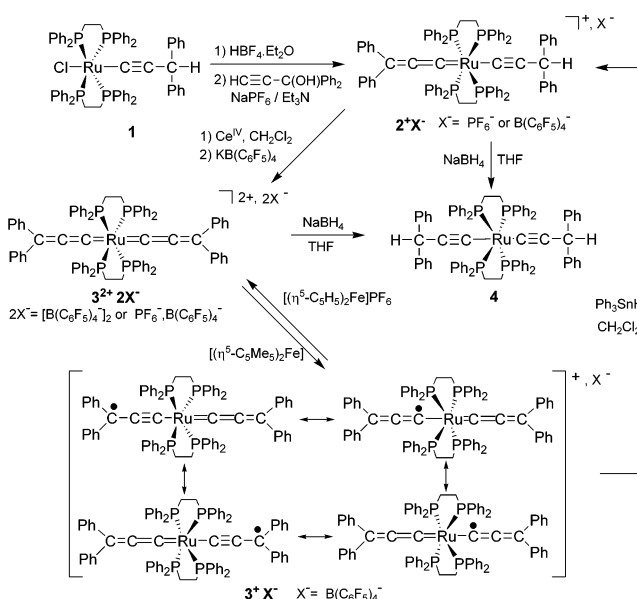
in CH_2Cl_2, shows a broad charge-transfer band with an intense absorbance ($\lambda_{max} = 618$ nm, $\epsilon = 80\,000$ mol^{-1} L cm^{-1}).[9] Hydride transfer to $3^{2+}[B(C_6F_5)_4^-]_2$ was achieved with NaBH$_4$ in THF to confirm the allenylidene structure. Thus, the reaction yielded the bis(alkynyl) ruthenium **4**, similarly obtained from **2**, and corresponds to the nucleophilic addition of two H$^-$ at the C_γ atoms.

Cyclic voltammetry of $3^{2+}[B(C_6F_5)_4^-]_2$ (0.1 M Bu$_4$NPF$_6$ in CH_2Cl_2) shows two well-defined one-electron reversible reduction waves at $E°_1 = -0.30$ V and $E°_2 = -0.93$ V vs ferrocene. The large separation of the reduction processes ($\Delta E° = 630$ mV, coproportionation constant $K_c = \exp(\Delta E°F/RT) = 7 \times 10^{10}$)[3a] allowed observation of the singly reduced species. We attempted to generate this reduced species in situ, allowing further spin trapping experiments or ESR spectroscopy investigations. Thus, addition of the reducing agent decamethylferrocene ($E° = -0.59$ V vs ferrocene) to $3^{2+}[B(C_6F_5)_4^-]_2$ selectively induces the first reduction process and affords in CH_2Cl_2 the blue cationic compounds $3^+B(C_6F_5)_4^-$. To quench this new radical, further addition of Ph$_3$SnH leads to $2^+B(C_6F_5)_4^-$ by selective addition of H$^•$ at the C_γ carbon atom (Scheme 1). Achieving the monoreduction of complex $3^{2+}[B(C_6F_5)_4^-]_2$ in a sealed ESR tube by dropping a crystal of decamethylferrocene in a THF solution allows the direct ESR observation of the radical species with a strong and persistent signal at 293 K with $g = 1.9972$ (Figure 1).[10] The trapping experiment supports the localization of the single electron on the trisubstituted carbon atoms, but the observed quintet with a coupling constant
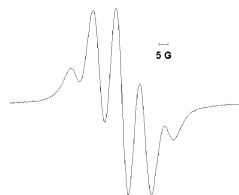
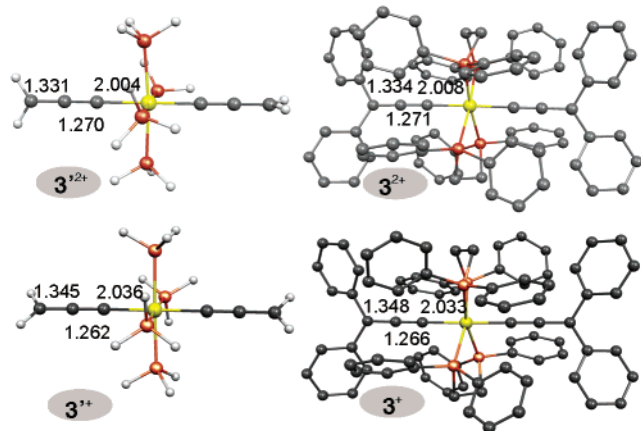**Figure 1.** ESR spectra of **3**$^+$ ($g = 1.9972$).

Figure 2. Optimized geometries of **3′**$^{n+}$ and **3**$^{n+}$ ($n = 1, 2$). Distances are given in Å.

$a_p = 13.5$ G (vs 3.0 G for *trans*-[Cl(dppe)$_2$Ru=C=C=CMe$_2$]PF$_6$)^{6a} due to the coupling of the single electron with the four equivalent phosphorus atoms suggests that it localizes closer to the metal than in the reduced ruthenium mono(allenylidene) as sketched by the second mesomeric form (Scheme 1). The IR studies, recorded in CH$_2$Cl$_2$, show the vanishing of the allenylidene band upon reduction with a slight excess of decamethylferrocene and the concomitant formation of a broad absorption at 1751 cm^{-1}. The absences of an allenylidene vibration stretch and of another stretch above 2000 cm^{-1}, characteristic of alkynyl species issued from allenylidene reduction,^{6d} rule out the hypothesis of a single electron located on only one carbon chain. Hence, these observations show that the electron is delocalized over the two chains rather on the carbon atoms close to the ruthenium.

Full DFT geometry optimization^{11} without any symmetry constraint of the simplified model [*trans*-(PH$_3$)$_4$Ru(=C=C=CH$_2$)$_2$]$^{2+}$ (**3′**$^{2+}$) leads to the bis(allenylidene) structure shown in Figure 2 with consistent allenylidene bond lengths.^{2e,6c} As expected from the isolobal analogy with all-carbon chains, the C$_\gamma$H$_2$ planes are perpendicular. However, it takes only 0.28 eV to bring them coplanar. QM(DFT)/MM geometry optimizations^{12} of **3**$^{2+}$ lead to a similar structure except that it exhibits a torsion angle of 27° between the C$_\gamma$Ph$_2$ planes. Geometry optimizations of the first reduced states **3′**$^+$ and **3**$^+$ at the DFT and QM/MM levels, respectively, lead to similar structures, with symmetrical carbon chains and torsion angles of 0 and 4°, respectively (Figure 2). Single-point DFT calculations^{11} on these optimized geometries found spin density concentrated on C$_\alpha$ (0.30 and 0.23, respectively) and C$_\gamma$ (0.40 and 0.25, respectively). The experimentally observed shift upon reduction of the IR allenylidene band (172 cm^{-1}) is in reasonable agreement with the corresponding calculated QM(DFT)/MM vibrational frequencies considering the level of theory (1982 and 1884 cm^{-1} for **3**$^{2+}$ and **3**$^+$, respectively). Thus, all our results are consistent with a delocalization of the single electron over both chains linked by the ruthenium atom, and especially on the C$_\alpha$ and C$_\gamma$ carbon atoms.

In conclusion, an original synthesis has been developed to obtain the first real bis(allenylidene) metal complex. The reduction affords a stable radical with the first evidence of an unpaired electron delocalized identically over the two carbon-rich chains. This study shows the potential of ruthenium bis(allenylidene) systems as connecting carbon-rich systems to mediate electron conduction.

Supporting Information Available: Experimental Section, selected DFT-optimized structural parameters of **3′**$^{n+}$ and **3**$^{n+}$ ($n = 1, 2$), and spin density distribution of **3′**$^+$ and **3**$^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) (a) Aviram, A.; Ratner, M. *Chem. Phys. Lett.* **1974**, *29*, 277. (b) Lehn, J.-M. *Supramolecular Chemistry: Concepts and Perspectives*; VCH: Weinheim, 1995, Chapter 8. (c) Long, N. J. In *Optoelectronic Properties of Inorganic Compounds*; Roundhill, D. M., Fackler, J. P., Eds.; Plenum Press: New York, 1999. (d) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555. (e) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

(2) (a) Wong, K.-T.; Lehn, J.-M.; Peng, S.-M.; Lee, G.-H. *Chem. Commun.* **2000**, 2259. (b) Xu, G.; Ren, T. *Organometallics* **2001**, *20*, 2400. (c) Gil-Rubio, J.; Weberndörfer, B.; Werner, H. *Angew. Chem., Int. Ed.* **2000**, *39*, 786. (d) Qi, H.;, Sharma, S.; Li, Z.; Snider, S. L.; Orlov, A. O.; Lent, C. S.; Fehlner, T. P. *J. Am. Chem. Soc.* **2003**, *125*, 15251. (e) Touchard, D.; Haquette, P.; Daridor, A.; Romero, A.; Dixneuf, P. H. *Organometallics* **1998**, *17*, 3844.

(3) (a) Paul, F.; Lapinte, C. *Coord. Chem. Rev.* **1998**, *178−180*, 431. (b) Dembinski, R.; Bartik, T.; Bartik, B.; Jaeger, M.; Gladysz, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 810. (c) Xu, G.-L.; Zou, G.; Ni, Y.-H.; DeRosa, M. C.; Crutchley, R. J.; Ren, T. *J. Am. Chem. Soc.*, **2003**, *125*, 10057. (d) Bruce, M. I.; Ellis, B. G.; Low, P. J.; Skelton, B. W.; White, A. H. *Organometallics* **2003**, *22*, 3184.

(4) Weng, W.; Bartik, T.; Brady, M.; Bartik, B.; Ramsden, J. A.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1995**, *117*, 11922. Mayor, M.; Von Hänish, C.; Webr, H. B.; Reichert, J.; Beckmann, D. *Ang. Chem., Int. Ed.* **2002**, *41*, 1183. Bruce, M. I.; Halet, J.-F.; Le Guennic, B.; Skelton, B. W.; Smith, M. E.; White, A. H. *J. Inorg. Chim. Acta* **2003**, *350*, 175. Yip, H. K.; Wu, J.; Wong, K.-Y.; Yeunh, K.-W.; Vitall, J. J. *Organometallics* **2002**, *21*, 1612.

(5) (a) Zhu, Y.; Clot, O.; Wolf, M. O.; Yap, G. P. A *J. Am. Chem. Soc.* **1998**, *120*, 1812. (b) Lebreton, C.; Touchard, D.; Le Pichon, L.; Daridor, A.; Toupet, L.; Dixneuf, P. H. *Inorg. Chim. Acta.* **1998**, *272*, 188.

(6) (a) Rigaut, S.; Maury, O.; Touchard, D.; Dixneuf, P. H. *Chem. Commun.* **2001**, 373. (b) Rigaut, S.; Monnier, F.; Mousset, F.; Touchard, D.; Dixneuf, P. H. *Organometallics* **2002**, *21*, 2657. (c) Auger, N.; Touchard, D.; Rigaut, S.; Halet, J.-F.; Saillard, J.-Y. *Organometallics* **2003**, *22*, 1638. (d) Winter, R. F.; Hartmann, S.; Zalis, S.; Klinkhammer, K. W. *J. Chem. Soc., Dalton Trans.* **2003**, 2342.

(7) An early attempt to prepare a bis(allenylidene), via an elimination reaction, led to the *trans*-(dppm)$_2$Ru[=C=C=C(OMe)(CH=CPh$_2$)]$_2^{2+}$ ↔ *trans*-(dppm)$_2$Ru[−C≡C−C(=OMe)(C=CPh$_2$)]$_2^{2+}$ with an elevated bis(alkynyl) character due to the presence of a donor group on the unsaturated chain ($\nu_{−C=C=C} = 1958$ cm^{-1}, C$_\alpha$ resonance is $\delta = 233.7$ ppm); see: Pirio, N.; Touchard, D.; Dixneuf, P. H.; Fettouhi, M.; Ouahab, L. *Angew. Chem., Int. Ed.* **1992**, *31*, 651.

(8) Selegue, J. P. *Organometallics* **1982**, *1*, 217.

(9) For complex **2**$^+$**PF$_6^-$**, $\lambda_{max} = 528$ nm, $\epsilon = 14\,000$ mol^{-1} L cm^{-1}.

(10) It has to be noted that reductions followed by reoxidation 30 min later with ferrocenium salt led to the regeneration of pure **3**$^{2+}$.

(11) All DFT calculations employed the Amsterdam Density Functional package, version 2002.01, with the PW91 functional (SCM, Theoretical Chemistry, Vrije Universiteit: Amsterdam, The Netherlands; http://www.scm.com). The atomic basis set used is a triple-Slater-type orbital (STO) + single-STO set (ADF basis set IV), with a frozen core approximation for the orbitals up to 1s for C, 2p for P, and 4p for Ru. Spin unrestricted formalism was used when needed.

(12) Geometries of **3**$^{n+}$ ($n = 1, 2$) were optimized using a QM/MM methodology implemented in the ADF package. The phenyl groups were described by molecular mechanics (MM) using the SYBYL/TRIPOS 5.2 force field constants (Clark, M.; Cramer, R. D. I., III; van Opdenbosch, N. *J. Comput. Chem.* **1989**, 982). The quantum mechanical (QM) part is represented by *trans*-(η^2-H$_2$PCH$_2$CH$_2$PH$_2$)$_2$Ru(=C=C=CH$_2$)$_2$, computed at the DFT level described in ref 11.

JA049631+