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One-pot palladium-catalysed synthesis of molecular wires

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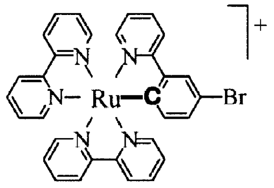
Abstract: *The one-pot desilylation of TMS-protected alcynes and cross-coupling with a brominated complex allows the use of sensitive diynes and provides an easy access to models of molecular wires.* © 1998 Published by Elsevier Science Ltd. All rights reserved.

Long-range electronic interaction between metallic centres or electrodes and its possible modulation are the basic principles of molecular electronics.[1] A chemical approach of this domain is the study of mixed valence complexes. Indeed, from the enveloppe of intervalence band lying in the near infrared region, regarded as an optically induced electron transfer (metal-to-metal charge transfer) through the bridging ligand, it is possible to extract the coupling parameter V_{ab}. Hence, a simple spectro-photometric study is necessary to obtain a quantitative result.[2]

Various families of compounds have been tested and most of the reported studies focused more on the role of the metallic centres or on the influence of the organic bridge's length on the global coupling.[3,4] However, the molecular structure-electronic interaction relationship is not clearly understood. To achieve such a goal, a versatile synthesis which could be adapted to various organic spacers, as well as an easy entry to dinuclear complexes are required, the final molecule having a fully conjugated rigid backbone.



1

The building blocks approach involving prefunctionnalised complexes is the best route in order to have the largest structural variations.[5,6] Recently we have described a new organometallic ruthenium complex **1** with a N_5C donor set easily prepared in two steps from commercial chemicals and suitable for palladium catalysed couplings.[7] On the other hand, the very straightforward synthesis of polytolanes make them very attractive as conjugated spacers to study electron or energy transfer.[8,9] Furthermore, their electronic properties depend mostly on the nature of the aromatic residues included within the chain.

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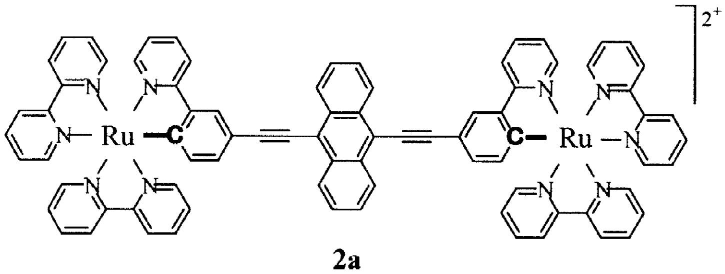
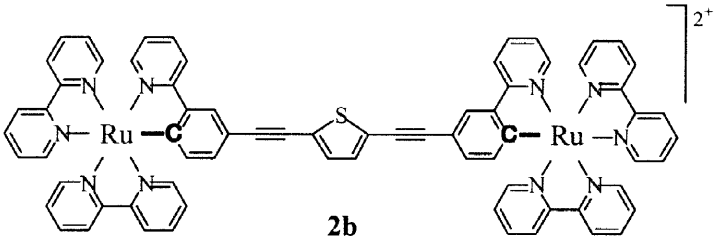
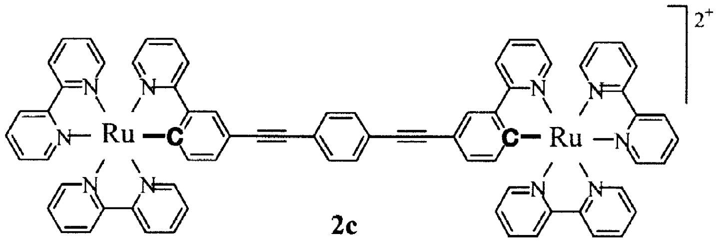
To understand the effect of the HOMO-LUMO gap of the bridging moiety on the coupling parameter V_{ab}, we decided to synthetise several molecules where only the aromatic bridge was changed from a small gap (anthracene **2a** or thiophene **2b**) to a large one (benzene **2c**).



2a



2b

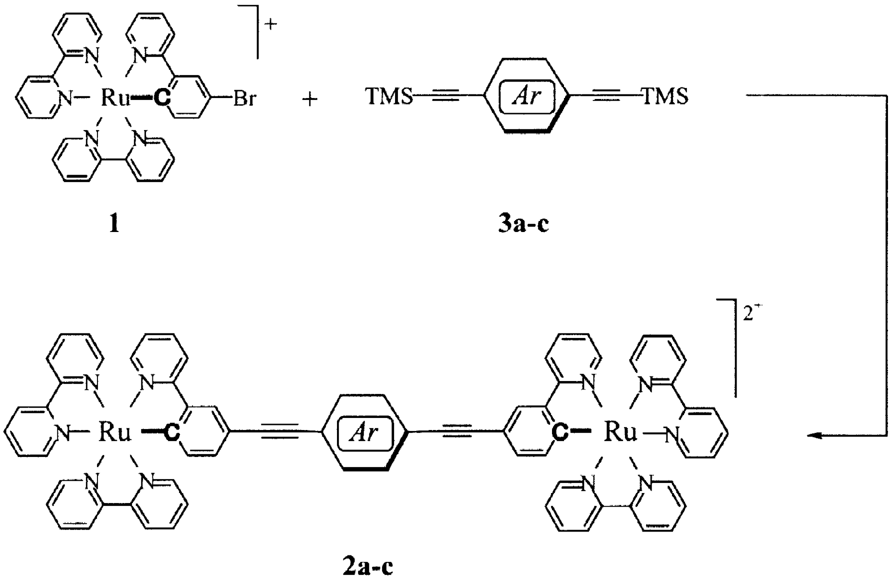


2c

Our initial strategy was to react an arene diyne with the complex **1** under the classic Sonogashira-Hagihara conditions (terminal dialkyne, Pd^{II}, CuI, organic amine as a base).[10] Poor results were obtained, and this failure was attributed to the diethynylarene unstability and to the already known low reactivity of complex **1**. Since alkyne desilylation and the palladium-catalysed tolane synthesis involve both a basic medium, we thought of an *in situ* deprotection, the free alkyne being used as soon as it is formed into the next step. Such a strategy has been already employed to couple acetone-protected alkynes with arylhalide under phase-transfer conditions.[11] Recently, desilylation followed by Eglinton oxidative dimerization of sensitive alkynes was also reported, the base being potassium carbonate in a methanol/pyridine mixture.[12]

Preliminary experiments using cesium fluoride in DMF led mostly to complex **1** degradation. However, sodium hydroxyde was found to be a very convenient reagent. Coupled products were obtained upon heating a DMF solution of disilanes **3a-c**,[13] complex **1**, and catalytic amounts of copper iodide and $Pd(PPh_3)_4$ in the presence of NaOH pellets for 16 hours at 80 °C (Scheme).[16] Yields were found to be moderate in the case of the very sensitive diynes 9,10-diethynylanthracene **3a** and 2,5-diethynylthiophene **3b**, to good with the 1,4-diethynylbenzene **3c**, which is more stable than the other two (Table). These results indicated that, despite the high nucleophilicity of the hydroxide ions, the release of the TMS group was slow enough compared to the rate of cross-coupling to ensure partial conversion of the free diyne into the desired dinuclear complexes. This was attributed to the poor solubility of NaOH pellets in the reaction mixture which were recovered almost unchanged after cooling down. The cationic complex **1**, substrate of the reaction, may act as a phase transfer agent for the hydroxyde ions, hence the reaction proceeds smoothly .

Spectroelectrochemical analysis of complexes **2a-c** have been performed. No splitting of the oxydation wave around 0.5 V (in MeCN, vs SCE) was found but the presence of a strong intervalence band was detected in the near infra red region for any complexes. As expected, the best V_{ab} value was found for **2a** (58 meV) and is even superior to values reported for similar cyclometallated complexes of the same length (about 21 angstroms).[4,17] Further details will be published elsewhere.



Scheme. *Reagents and conditions:* NaOH, CuI (3 %), $Pd(PPh_3)_4$ (5 %) DMF, 80 °C, 16 hrs.

Complex	Isolated yield
2a	34 %
2b	39 %
2c	60 %

Table.

We have shown that it is possible to couple poorly reactive arylbromides with very sensitive alkynes using the Sonogashira-Hagihara protocole and an *in situ* deprotection of a stable silane by sodium hydroxyde in DMF. These heterogeneous conditions, slowing down the desilylation step, where the cationic substrate may act as a phase-transfer agent, provide a concise route to a new familly of chemical models of molecular wires.

Acknowledgements

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References and notes

1- Joachim, C.; Launay, J.-P. *J. Mol. Electronics* **1990**, *6*, 37-50.

2- Ribou, A.-C.; Launay, J.-P.; Takahashi, K.; Nihira, T.; Tarutani, S.; Spangler, C.; *Inorg. Chem.* **1994**, *33*, 1325-1329.

3- Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc. Chem. Commun.* **1993**, 434-435.

4- Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 1775-1778.

5- Chodorowsky-Kimmes, S.; Beley, M.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1996**, *37*, 2963-2966.

6- Connors, P.; Tzalis, D.; Dunnick, A.; Tor, Y. *Inorg. Chem.* **1998**, *37*, 1121-1123.

7- Coudret, C.; Fraysse, S.; Launay, J.-P. *Chem. Commun.* **1998**, 663-664.

8- Hoshino, H.; Suzuki, T.; Umeda, H. *Inorganica Chimica Acta* **1996**, 245, 87-90.

9- Wagner, R.; Lindsey, J. *J. Am. Chem. Soc.* **1994**, *116*, 9759-9760.

10- Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467-4470.

11- Carpita, A.; Lessi, A.; Rossi, R. *Synthesis* **1984**, 571-572.

12- Haley, M.; Bell, M.; Brand, S.; Kimball, D.; Pak, J.; Wan, B. *Tetrahedron Let.* **1997**, *38*, 7483-7486.

13- The bis(trimethyl)silyl alkynes **3a-c** were synthetised by Sonogashira-Hagiharacross-coupling ($Pd(PPh_3)_4$, CuI, diisopropylamine, room temperature) between the corresponding diiodo-aromatic[14] compounds and trimethylsilylacetylene (yields in the range of 90 to 98 %).[15]

14- All chemicals were commercially available except 9,10-diiodoanthracene which was synthetised following Duerr, B.; Chung, Y.; Czarnik, A. *J. Am. Chem. Soc.*, **1988**, *53*, 2120-2122.

15- Huynh, C.; Linstrumelle, G. *Tetrahedron*, **1988**, *44*, 6337-6344.

16- A representative procedure is given as follow for **2a**. To a schlenk tube containing **1** (150 mg, 0.19 mmol) and **3a** (34 mg, 0.09 mmol) in anhydrous DMF is added ($Pd(PPh_3)_4$ (10 mg, 0.05 eq.), CuI (10 mg, 0.3 eq.) then one pellet (100 mg) of sodium hydroxide. After stirring under argon at 80 °C for 16 hours the solvent is removed in vacuo. The crude product is purified by chromatography on a silica gel semi-preparative plate (eluent toluene/acetonitrile (60/40), desorption with a concentrated solution of NH_4PF_6 in acetonitrile). Yield : 51 mg (34 %). All the complexes were characterized by ^{1}H-NMR, ESMS, spectroelectrochemistry and UV-Vis. spectroscopy.

Selected analytical data for **2a**: ^{1}H NMR (CD_3CN, 250 MHz): δ (ppm) vs TMS: 6.65 (d, J = 7.8, 2H), 7.02 (td, J = 6.5, 1.4, 1H), 7.21-7.29 (m, 8H), 7.44 (td, J = 6.5, 1.2, 2H), 7.64 (dd, J = 5.6, 0.8, 2H), 7.71 (dd, J = 6.8, 3.3, 4H), 7.74-7.91 (m, 16H), 8.01 (td, J = 7.9, 1.7, 2H), 8.1 (dd, J = 5.6, 0.8, 2H), 8.25 (d, J = 8.0, 2H), 8.30 (sd, J = 1.5, 2H), 8.33-8.43 (m, 6H), 8.48 (d, J = 8.2, 2H), 8.76 (dd, J = 6.7, 3.3, 4H). FAB-MS (NBA matrix m/z: 1503 $(M-PF_6)^+$ calcd 1502, 679 $(M-2\ PF_6)^{2+}$ calcd 678.7. UV-VIS (CD_3CN): λ_{max} (nm) (ε [$M^{-1}cm^{-1}$]): 535 (66806), 416 (30032), 360 (38122), 297 (159720), 261 (108972).

17- Patoux, C.; Launay, J.-P.; Beley, M.; Chodorowski-Kimmes, S.; Collin, J.-P.; James, S.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1998**, *120*, 3717-3725.

18- Balacco, J. *J. Chem. Comput. Sci.* **1994**, *34*, 1235.