Connecting C≡C Bonds to Tetrairidium Chains

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The rational design of electronic devices at molecular-scale, such as wires and switches, requires the development of precise synthetic procedures to tailor molecules suitable for electronic delocalization. Well-recognized building blocks for such purposes are oligomers from both, organic and organometallic chemistry. Among them, the fascinating properties of carbon-based materials like carbon nanotubes^[1] and conjugated polyenes^[2] have been intensively explored. In addition, the search for reproducible synthetic methodologies leading to molecular wires based on transition metal complexes has been the subject of an impressive effort. Metal atoms can be positioned in a linear array by the use of carefully designed ligands such as oligo- α -pyridyl/naphthyridyl amido ligands,^[3] which has allowed the isolation of linear metal chains ranging from three metals to the remarkable undecanickel string recently reported.^[4] Other different approaches are based on oxidation/reduction reactions of appropriate dinuclear complexes to render lineal oligomers with unsupported metal-metal bonds^[5] while multiply-bonded bimetallic units have been used as precursors for tetranuclear complexes with metal-metal bonds.^[6] Moreover, a combination of both types of building blocks, organic and organometallic ones, has been elegantly developed by Murahashi and Kurosawa^[7] for the synthesis of sandwich complexes with linear/bent palladium arrays and, from a different point of view, by Ren connecting dinuclear complexes to a wide range of conjugated polyenes.^[8] From this approach, motifs ranking from $\text{RC}\equiv\text{C}-[\text{Ru}_2]$ ^[9] to $\text{RC}\equiv\text{C}-[\text{Ru}_2]-\text{C}\equiv\text{CR}$,^[10] $[\text{Ru}_2]-(\text{C}\equiv\text{C})_n-[\text{Ru}_2]$,^[11] and the amazing hexametallic doubly connected wire $[\text{Ru}_2]-(\text{C}\equiv\text{C})_n-[\text{Ru}_2]-(\text{C}\equiv\text{C})_n-[\text{Ru}_2]$ ^[12] with strong intermetallic communication have been prepared ($[\text{Ru}_2] = \text{Ru}_2\text{L}_4$, L = binucleating ligand). Linear complexes of higher nuclearity have been comparatively less studied in this field; with only few reported examples of trinuclear compounds connected to acetylide units.^[13] Inspired in this work and from our experience in the synthesis of rhodium and iridium oligomers with the metals in fractional oxidation states,^[14] we decide to explore the possibility of connecting acetylide motifs to tetrairidium chains. As far as we know, such type of oligomers has not been used previously for this purpose.

One-electron oxidation of $[\text{Ir}_2(\mu\text{-OPy})_2(\text{CO})_4]$ (**1**, OPy = 2-pyridonate) with $[\text{FeCp}_2]\text{PF}_6$ in acetonitrile gives immediately the diamagnetic tetranuclear chain $[\text{MeCN}-\{\text{Ir}_4\}-\text{NCMe}](\text{PF}_6)_2$

($[\text{2}](\text{PF}_6)_2$, $\{\text{Ir}_4\} = [\{\text{Ir}_2(\mu\text{-OPy})_2(\text{CO})_4\}_2]^{2+}$), which was isolated in good yield (76 %) as a yellow-green solid on addition of diethyl ether. The X-ray crystal structure of **[2]**²⁺ (Figure 1, top)^[15] shows two face-to-face dinuclear iridium complexes with an H,H configuration bound by an unsupported Ir–Ir bond between the O,O-coordinated iridium atoms. The four metals display an almost lineal disposition with two acetonitrile molecules at both ends of the chain. The metals possess an average oxidation state +1.50, while both halves of the molecule are in a fully eclipsed conformation around the unsupported Ir–Ir bond (torsion angle around Ir1–Ir1' = 180°).

Figure 1. Structures (ORTEP at 50% level) of the tetranuclear cation **[2]**²⁺ (top) and the phenylacetylide tetranuclear cation **[3]**⁺ (bottom).

Addition of phenylacetylene to **[2](PF₆)₂** not only removes the labile acetonitrile ligands, but the reaction is accomplished by the spontaneous deprotonation of $\text{PhC}\equiv\text{CH}$ to become a σ -bonded phenylacetylide along with HPF_6 . The resulting diamagnetic tetranuclear chain $[\{\text{Ir}_4-\text{C}\equiv\text{CPh}\}]\text{PF}_6$ (**[3](PF₆)**) was isolated in good yield by carrying out the reaction in the presence of one mol-equiv of KO^tBu . A further addition of $\text{PhC}\equiv\text{CH}$ and base did not give the hypothetical diacetylide complex. The four metals and the carbon atoms of the acetylide group display a nearly lineal disposition in the X-ray structure of the cation **[3]**⁺ (Figure 1, bottom),^[15] in which the unsupported Ir–Ir bond distance was found to be similar to that in **[2]**²⁺ and the metals show again an average oxidation state +1.5.

Remarkably, the *trans*-influence of the alkynyl group is transmitted along the metallic chain, in such a way that the

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coordination position at the opposite metal in the chain (Ir4) is vacant. All attempts to model the hypothetical cation $[\text{MeCN}-\{\text{Ir}_4\}-\text{C}\equiv\text{CPh}]^+$ by DFT calculations systematically led to decoordination of acetonitrile, with a relative minimum of energy for a $\text{MeCN}-\text{Ir}4$ distance over 3.0 Å. Furthermore, there is a notable enlargement of the intra-dimer $\text{Ir}3-\text{Ir}4$ bond distance to 2.7935(7) Å in $[\mathbf{3}]^+$ relative to the similar one ($\text{Ir}1-\text{Ir}2$) in the same complex and to those observed in $[\mathbf{2}]^{2+}$ (nearly 2.69 Å). These data point out to important transference of electron density from the acetylide to the remote Ir4 center through the $\text{Ir}4-\text{Ir}3-\text{Ir}2-\text{Ir}1-\text{C}\equiv\text{CPh}$ backbone. Noticeably, the $\text{Ir}1-\text{C}29-\text{C}30$ linkage is almost lineal (177.8(2)°) in contrast with the significant bending observed in terminal acetylide complexes.^[9a]

Also remarkable is the stability found for these diamagnetic tetrairidium chains in solution where both remain intact, giving the expected resonances in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra. Thus, complex $[\text{MeCN}-\{\text{Ir}_4\}-\text{NCMe}]^{2+}$ ($[\mathbf{2}]^{2+}$) shows four equivalent α -pyridonate groups, while the acetylide complex $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPh}]^+$ ($[\mathbf{3}]^+$) displays two non-equivalent α -pyridonate bridging ligands along with the resonances corresponding to the $[\text{PhC}^\alpha=\text{C}^\beta-\text{Ir}1]$ fragment (see Supporting Information). Complexes $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^+$ as well as $[\mathbf{4}]^{2+}$ (see below) do not show bands in the near-IR region (2500–800 nm), as expected for very strong electronic coupling between the metals, and hence they fit in the Robin and Day Class III compounds.^[16]

CV measurements of the acetonitrile solvate $[\text{MeCN}-\{\text{Ir}_4\}-\text{NCMe}]^{2+}$ ($[\mathbf{2}]^{2+}$) show an irreversible oxidation process at very high potential (+1.56 V versus SCE) and two irreversible reduction processes at −0.33 and −1.54 V, respectively. Major difference in the CV of $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPh}]^+$ ($[\mathbf{3}]^+$) relative to $[\mathbf{2}]^{2+}$ is the appearance of a new irreversible oxidation wave at lower potential (+0.82 V, see Supporting Information). To clearly establish the origin of this variation, DFT calculations on $[\mathbf{2}]^{2+}$ and $[\mathbf{3}]^+$ were carried out. The bond lengths and angles of the $\{\text{Ir}_4\}$ core in the optimized geometries match well with those from the crystal structures. Selected MOs of both compounds are shown in Figure 2. The HOMO and LUMO for complex $[\mathbf{2}]^{2+}$ are both mainly metal-centred molecular orbitals corresponding to two of the four combinations of the iridium d_z^2 orbitals (Figure 2, left). The HOMO shows a bonding character for the inter-dimer $\sigma-\text{Ir}2-\text{Ir}2'$ bond and antibonding nature for the intra-dimer metal interactions, while the LUMO develops an antibonding character between every pair of adjacent iridium atoms. The electron vacancy of this high-energy σ MO is the responsible for the stability of the unsupported metal-metal bond between the two dinuclear moieties. Interestingly, the HOMO of complex $[\mathbf{3}]^+$ (Figure 3, right) is essentially the ligand-centred π -orbital of $\text{C}\equiv\text{CPh}$ while the HOMO−1 corresponds to a molecular orbital similar to the HOMO of $[\mathbf{2}]^{2+}$. The main difference between the HOMO of $[\mathbf{2}]^{2+}$ and the HOMO−1 of $[\mathbf{3}]^+$ is the alteration of the bonding/antibonding sequence in the chain. Thus, the bonding interaction was found at the unsupported $\text{Ir}2-\text{Ir}2'$ bond in $[\mathbf{2}]^{2+}$, but at the intra-dimer $\text{Ir}1-\text{Ir}2$ bond in $[\mathbf{3}]^+$. The LUMO is of the same type for both complexes.

Figure 2. Selected MOs of complexes $[\text{MeCN}-\{\text{Ir}_4\}-\text{NCMe}]^{2+}$ ($[\mathbf{2}]^{2+}$) (left) and $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPh}]^+$ ($[\mathbf{3}]^+$) (right) from DFT calculations. Hydrogen atoms have been omitted for clarity (see Supporting Information for details).

The gaps HOMO–LUMO in $[\mathbf{2}]^{2+}$ and HOMO−1–LUMO in $[\mathbf{3}]^+$ display similar values (2.956 eV and 2.906 eV, respectively), which can be expected from the analogous nature of both MOs. Noticeably, the HOMO–LUMO gap in $[\mathbf{3}]^+$ becomes reduced up to 2.720 eV because of the presence of the $\pi-\text{C}\equiv\text{CPh}$ MO. The intercalation of this MO (mainly ligand centred) should be the origin of the lower first oxidation potential found for $[\mathbf{3}]^+$ relative to that of $[\mathbf{2}]^{2+}$.

According to the above description, one-electron oxidized species, $[\mathbf{2}]^{\bullet 3+}$ and $[\mathbf{3}]^{\bullet 2+}$, could in principle expected to be radicals with the unpaired electron delocalized in the metallic chain and in the phenylacetylide moiety, respectively. DFT calculations for $[\mathbf{2}]^{\bullet 3+}$ show indeed that the SOMO is analogous to the HOMO of $[\mathbf{2}]^{2+}$. However, these calculations for $[\mathbf{3}]^{\bullet 2+}$ revealed that abstraction of one-electron from $[\mathbf{3}]^+$ is accompanied by a full mixing of the original HOMO and HOMO−1 of $[\mathbf{3}]^+$ in such a way that a new bonding/anti-bonding pair is produced. Consequently, the resulting SOMO and LUMO of $[\mathbf{3}]^{\bullet 2+}$ show almost similar contributions from the iridium chain and the phenylacetylide ligand. Figure 3 displays the spin density plot of paramagnetic $[\mathbf{3}]^{\bullet 2+}$, which shows the full delocalization of the unpaired electron over the $\text{Ir}4-\text{Ir}3-\text{Ir}2-\text{Ir}1-\text{C}\equiv\text{CPh}$ backbone providing a σ -‘metal-organic-road’ for the free movement of the electron.

Figure 3. Spin density of the paramagnetic species $[\mathbf{3}]^{\bullet 2+}$ from DFT calculations. α spin density is in blue while β spin density is in green. Hydrogen atoms have been omitted for clarity (see Supporting Information for details).

The bis(acetylene) 1,4-bis(ethynyl)benzene duplicates well the above described reaction allowing the connection of two tetrametallic chains to produce the octanuclear complex $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPhC}\equiv\text{C}-\{\text{Ir}_4\}](\text{PF}_6)_2$ ($[\mathbf{4}](\text{PF}_6)_2$). The reaction takes place stepwise through the tetranuclear intermediate $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPhC}\equiv\text{CH}](\text{PF}_6)$ ($[\mathbf{5}]\text{PF}_6$). Analytical and spectroscopic data for $[\mathbf{4}](\text{PF}_6)_2$ and $[\mathbf{5}]\text{PF}_6$ corroborated the proposed formulations. Relevant resonances for the remarkable octametallic chain $[\{\text{Ir}_4\}-\text{C}\equiv\text{CPhC}\equiv\text{C}-\{\text{Ir}_4\}](\text{PF}_6)_2$ are one sharp singlet for the four

equivalent protons and two signals for the carbons of the phenyl group in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, respectively. Moreover, the octanuclear nature of $\{[\text{Ir}_4]-\text{C}\equiv\text{CPhC}\equiv\text{C}-[\text{Ir}_4]\}^{2+}$ is maintained in solution, as deduced from pulsed gradient spin-echo (PGSE) NMR diffusion (DOSY) spectra. Thus, the tetrairidium chains $[2]^{2+}$ and $[3]^+$ show diffusion coefficients (D) of 9.487×10^{-10} and $9.941 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively, while D for the octanuclear chain $[4]^{2+}$ is $6.858 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$. From these data, the hydrodynamic radius were found to be 5.95, 5.68 and 8.23 Å for $[2]^{2+}$, $[3]^+$ and $[4]^{2+}$, respectively, which match the average radius estimated from X-ray and DFT structures (5.98, 5.84 and 8.29 Å for $[2]^{2+}$, $[3]^+$ and $[4]^{2+}$, respectively).^[17] Furthermore, the monocation ($m/z = 2862.9$) for $[4]^{2+}$ was detected in the MALDI-TOF+ spectrum (see Supporting Information).

Since no single crystals of $[4]^{2+}$ of appropriate size could be grown,^[18] its structure was modelled by DFT methods. On the whole, it corresponds to a duplication of the above one described for the cation $\{[\text{Ir}_4]-\text{C}\equiv\text{CPh}\}^+ ([3]^+)$, exhibiting an almost linear $\text{Ir4a}-\text{Ir3a}-\text{Ir2a}-\text{Ir1a}-\text{C}\equiv\text{CPhC}\equiv\text{C}-\text{Ir1b}-\text{Ir2b}-\text{Ir3b}-\text{Ir4b}$ backbone with a length of around 3 nm from Ir4a to Ir4b. The octametallic chain also shows an enlargement of the $\text{Ir3a}-\text{Ir4a}$ and $\text{Ir3b}-\text{Ir4b}$ bond distances (2.896 Å in both cases) relative those in the dinuclear moiety bound to the acetylide ligand, $\text{Ir1a}-\text{Ir2a}$ and $\text{Ir1b}-\text{Ir2b}$ (2.733 and 2.734 Å, respectively). It is not surprising that inclusion of the 'C≡CPhC≡C' fragment between two $\{\text{Ir}_4\}$ chains also produces a HOMO mainly π -delocalized on the organic linker (Figure 4, top). The LUMO and LUMO+1 are almost equal in energy ($\Delta E = 0.0019 \text{ eV}$), being both almost identical to the LUMO described for $\{[\text{Ir}_4]-\text{C}\equiv\text{CPh}\}^+$; one of them develops an antibonding character in the tetrametallic chain on the left (from Ir1a to Ir4a) and the other one in that on the right (from Ir1b to Ir4b). A similar situation occurs for the HOMO-1 and HOMO-2 ($\Delta E = 0.0025 \text{ eV}$); the former shows a bonding character for the $\text{Ir1a}-\text{Ir2a}$ interaction while the bonding character is found for the $\text{Ir1b}-\text{Ir2b}$ interaction in the latter (see Supporting Information).

Figure 4. HOMO of $\{[\text{Ir}_4]-\text{C}\equiv\text{CPhC}\equiv\text{C}-[\text{Ir}_4]\}^{2+}$ ($[4]^{2+}$) (top) and spin density of the paramagnetic species $[4]^{3+}$ (bottom) from DFT calculations. α spin density is in blue while β spin density is in green. Hydrogen atoms have been omitted for clarity (see Supporting Information for details).

Cyclic voltammetry of $\{[\text{Ir}_4]-\text{C}\equiv\text{CPhC}\equiv\text{C}-[\text{Ir}_4]\}(\text{PF}_6)_2$ was found to be basically similar to that above described for $\{[\text{Ir}_4]-\text{C}\equiv\text{CPh}\}^+ ([3]^+)$. Two fully irreversible waves at 0.85 and 1.44 V were observed in the oxidation region while a fully irreversible wave at -1.04 V was present in the cathodic region. The first oxidation wave could correspond to the formation of the radical

$\{[\text{Ir}_4]-\text{C}\equiv\text{CPhC}\equiv\text{C}-[\text{Ir}_4]\}^{\bullet 3+}$ whose SOMO (Figure 4, bottom) shows almost similar contributions from the two iridium chains and the diphenylacetylide ligand.

In summary, we report novel iridium chains linked to acetylide moieties for which electrochemical and DFT studies are indicative of extensive σ -delocalization between metals and linkers. The strong modification that the organic linker provides to the HOMOs of the tetranuclear chains is remarkable. For the acetonitrile complex $[\text{MeCN}-\{\text{Ir}_4\}-\text{NCMe}]^{2+}$ the HOMO is mainly a σ -delocalized metal-based orbital, while on connecting the phenylacetylide ligands the HOMOs of the oligomers became π -delocalized and ligand-centred molecular orbitals. Moreover, the full delocalization of the unpaired electron over the σ - $\text{Ir4a}-\text{Ir3a}-\text{Ir2a}-\text{Ir1a}-\text{C}\equiv\text{CPhC}\equiv\text{C}-\text{Ir1b}-\text{Ir2b}-\text{Ir3b}-\text{Ir4b}$ backbones found in $[3]^{\bullet 2+}$ and $[4]^{\bullet 3+}$ shed light on the possible use of these type of molecules as 'molecular wires' in which appropriate combinations of metal and ligands provide unexpected roads for electrons. The latter represents a unique example of organic/metallic electronic communication spanning around 30 Å. Further work on ligand engineering to create different iridium oligomers and longer wires is currently being developed in our laboratory.

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- [1] a) W. J. Yu, Y. H. Lee, *ChemSusChem* **2011**, *4*, 890–904; b) E. Raymundo-Piñero, M. Cadek, M. Wachtler, F. Béguin, *ChemSusChem* **2011**, *4*, 943–949; c) P. Wick, M. J. D. Clift, M. Rösslein, B. Rothen-Rutishauser, *ChemSusChem* **2011**, *4*, 905–911; d) G. Centi, S. Perathoner, *ChemSusChem* **2011**, *4*, 913–925; e) X. Pan, X. Bao, *Acc. Chem. Res.* **2011**, *44*, 553–562; f) R. L. Carroll, C. B. Gorman, *Angew. Chem.* **2002**, *114*, 4556–4579; *Angew. Chem. Int. Ed.* **2002**, *41*, 4378–4400; g) J. M. Tour, *Acc. Chem. Res.* **2000**, *33*, 791–804; h) F. Paul, C. Lapinte, *Coord. Chem. Rev.* **1998**, *178–180*, 431–509.
- [2] a) M. Kivala, F. Diederich, *Acc. Chem. Res.* **2009**, *42*, 235–248; b) Y. M. Zhao, N. Z. Zhou, A. D. Slepov, S. C. Ciulei, R. McDonald, F. A. Hegmann, R. R. Tykwinski, *Helv. Chim. Acta* **2007**, *90*, 909–927.
- [3] a) W.-Z. Wang, R. H. Ismayilov, G.-H. Lee, Y.-L. Huang, C.-Y. Yeh, M.-D. Fu, C.-h. Chen, S.-M. Peng, *New. J. Chem.* **2012**, *36*, 632–637; b) J.-H. Kuo, T.-B. Tsao, G.-H. Lee, H.-W. Lee, C.-Y. Yeh, S.-M. Peng, *Eur. J. Inorg. Chem.* **2011**, 2025–2028; c) S.-A. Hua, G.-C. Huang, I. P.-C. Liu, J.-H. Kuo, C.-H. Jiang, C.-L. Chiu, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Chem. Commun.* **2010**, *46*, 5018–5020; d) K.-N. Shih, M.-J. Huang, H.-C. Lu, M.-D. Fu, C.-K. Kuo, G.-C. Huang, G.-H. Lee, C.-H. Chen, S.-M. Peng, *Chem. Commun.* **2010**, *46*, 1338–1340; e) S.-A. Hua, I. P.-C. Liu, H. Hasanov, G.-C. Huang, R. H. Ismayilov, C.-L. Chiu, C.-Y. Yeh, G.-H. Lee, S.-M. Peng, *Dalton Trans.* **2010**, *39*, 3890–3896; f) I. P.-C. Liu, C.-F. Chen, S.-A. Hua, C.-H. Chen, H.-T. Wang, G.-H. Lee, S.-M. Peng, *Dalton Trans.* **2009**, 3571–3573; g) Y. Takemura, T. Nakajima, T. Tanase, M. Usuki, H. Takenaka, E. Goto, M. Mikuriya, *Chem. Commun.* **2009**, 1664–1666; h) I. P.-C. Liu, W.-Z. Wang, S.-M. Peng, *Chem. Comm.* **2009**, 4323–4331 and references therein; i) F. A. Cotton, C. A. Murillo, Q. Wang, M. D. Young, *Eur. J. Inorg. Chem.* **2008**, 5257–5262 and references therein; j) C. Yin,

- G.-C. Huang, C.-K. Kuo, M.-D. Fu, H.-C. Lu, J.-H. Ke, K.-N. Shih, Y.-L. Huang, G.-H. Lee, C.-Y. Yeh, C.-H. Chen, S.-M. Peng, *J. Am. Chem. Soc.* **2008**, *130*, 10090–10092.
- [4] R. H. Ismayilov, W.-Z. Wang, G.-H. Lee, C.-Y. Yeh, S.-A. Hua, Y. Song, M.-M. Rohmer, M. Bénard, S.-M. Peng, *Angew. Chem.* **2011**, *123*, 2093–2096; *Angew. Chem. Int. Ed.* **2011**, *50*, 2045–2048.
- [5] For general perspectives and recent examples see for example: a) M. G. Campbell, D. C. Powers, J. Raynaud, M. J. Graham, P. Xie, E. Lee, T. Ritter, *Nature Chem.* **2011**, *3*, 949–953; b) K. Uemura, K. Fukui, K. Yamasaki, K. Matsumoto, M. Ebihara, *Inorg. Chem.* **2010**, *49*, 7323–7330 and references therein; c) S. Arai, M. Ochiai, K. Ishihara, K. Matsumoto, *Eur. J. Inorg. Chem.* **2007**, 2031–2039; d) J. K. Bera, K. R. Dunbar, *Angew. Chem.* **2002**, *114*, 4633–4637; *Angew. Chem. Int. Ed.* **2002**, *41*, 4453–4457; e) C. Tejel, M. A. Ciriano, L. A. Oro, *Chem. Eur. J.* **1999**, *5*, 1131–1135; f) T. O. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts, S. J. Lippard, *Inorg. Chem.* **1987**, *26*, 1261–1270; g) T. O. O'Halloran, M. M. Roberts, S. J. Lippard, *J. Am. Chem. Soc.* **1984**, *106*, 6427–6428; h) P. K. Mascharak, I. D. Williams, S. J. Lippard, *J. Am. Chem. Soc.* **1984**, *106*, 6428–6430.
- [6] a) K. Pal, K. Nakao, K. Mashima, *Eur. J. Inorg. Chem.* **2010**, 5668–5674; b) K. Mashima, *Bull. Chem. Soc. Jpn.* **2010**, *83*, 299–312 and references therein.
- [7] a) T. Murahashi, K. Shirato, A. Fukushima, K. Takase, T. Suenobu, S. Fukuzumi, S. Ogoshi, H. Kurosawa, *Nature Chem.* **2012**, *4*, 52–58; b) T. Murahashi, Y. Mino, K. Chiyoda, S. Ogoshi, H. Kurosawa, *Chem. Commun.* **2008**, 4061–4063; c) Y. Tatsumi, T. Murahashi, M. Okada, S. Ogoshi, H. Kurosawa, *Chem. Commun.* **2008**, 477–479; d) T. Murahashi, N. Kato, T. Uemura, H. Kurosawa, *Angew. Chem.* **2007**, *119*, 3579–3583; *Angew. Chem. Int. Ed.* **2007**, *46*, 3509–3512; e) Y. Tatsumi, K. Shirato, T. Murahashi, S. Ogoshi, H. Kurosawa, *Angew. Chem.* **2006**, *118*, 5931–5935; *Angew. Chem. Int. Ed.* **2006**, *45*, 5799–5803.
- [8] T. Ren, *Organometallics* **2005**, *24*, 4854–4870 and references therein.
- [9] See for example: a) S. P. Cummings, Z. Cao, C. W. Liskey, A. R. Geanes, P. E. Fanwick, K. M. Hassell, T. Ren, *Organometallics* **2010**, *29*, 2783–2788; b) L. Zhang, B. Xi, I. P.-C. Liu, M. M. R. Choudhuri, R. J. Crutchley, J. B. Updegraff, J. D. Protasiewicz, T. Ren, *Inorg. Chem.* **2009**, *48*, 5187–5194; c) M. Nguyen, T. Phan, E. V. Caemelbecke, W. Kajonkijya, J. L. Bear, K. M. Kadish, *Inorg. Chem.* **2008**, *47*, 7775–7783; d) A. S. Blum, T. Ren, D. A. Parish, S. A. Trammell, M. H. Moore, J. G. Kushmerick, G.-L. Xu, J. R. Deschamps, S. K. Pollack, R. Shashidhar, *J. Am. Chem. Soc.* **2005**, *127*, 10010–10011; e) A. R. Chakravarty, F. A. Cotton, *Inorg. Chim. Acta* **1986**, *113*, 19–26.
- [10] a) W. P. Forrest, Z. Cao, P. E. Fanwick, K. M. Hassell, T. Ren, *Organometallics* **2011**, *30*, 2075–2078; b) I. P.-C. Liu, T. Ren, *Inorg. Chem.* **2009**, *48*, 5608–5610; c) B. Xi, G.-L. Xu, P. E. Fanwick, T. Ren, *Organometallics* **2009**, *28*, 2338–2341; d) J.-W. Ying, A. Córdova, T. Y. Ren, G.-L. Xu, T. Ren, *Chem. Eur. J.* **2007**, *13*, 6874–6882; e) G.-L. Xu, R. J. Crutchley, M. C. DeRosa, Q.-J. Pan, H.-X. Zhang, X. Wang, T. Ren, *J. Am. Chem. Soc.* **2005**, *127*, 13354–13363; f) G.-L. Xu, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem. Soc.* **2004**, *126*, 3728–3729.
- [11] a) B. Xi, I. P.-C. Liu, G.-L. Xu, M. M. R. Choudhuri, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem. Soc.* **2011**, *133*, 15094–15104; b) Y. Fan, I. P.-C. Liu, P. E. Fanwick, T. Ren, *Organometallics* **2009**, *28*, 3959–3962; c) Y. Shi, G. T. Yee, G. Wang, T. Ren, *J. Am. Chem. Soc.* **2004**, *126*, 10552–10553; d) G.-L. Xu, G. Zou, Y.-H. Ni, M. C. DeRosa, R. J. Crutchley, T. Ren, *J. Am. Chem. Soc.* **2003**, *125*, 10057–10065; e) T. Ren, G. Zo, J. C. Álvarez, *Chem. Commun.* **2000**, 1197–1198.
- [12] a) J.-W. Ying, I. P.-C. Liu, B. Xi, Y. Song, C. Campana, J.-L. Zuo, T. Ren, *Angew. Chem.* **2010**, *122*, 966–969; *Angew. Chem. Int. Ed.* **2010**, *49*, 954–957.
- [13] [Ni₃]: a) F. A. Cotton, H. Chao, Z. Li, C. A. Murillo, Q. Wang, *J. Organomet. Chem.* **2008**, *693*, 1412–1419; b) J. F. Berry, F. A. Cotton, C. A. Murillo, *Dalton Trans.* **2003**, 3015–3021; [Co₃]: c) J. F. Berry, F. A. Cotton, C. A. Murillo, *Organometallics* **2004**, *23*, 2503–2506; [Cr₃]: d) R. Clérac, F. A. Cotton, L. M. Daniels, K. R. Dunbar, C. A. Murillo, I. Pascual, *Inorg. Chem.* **2000**, *39*, 748–751; e) J. F. Berry, F. A. Cotton, C. A. Murillo, B. K. Roberts, *Inorg. Chem.* **2004**, *43*, 2277–2283; [Ru₃]: f) C.-K. Kuo, J.-C. Chang, C. Y. Yeh, G. H. Lee, C.-C. Wang, S.-M. Peng, *Dalton Trans.* **2005**, 3696–3701.
- [14] a) B. E. Villarroya, C. Tejel, M.-M. Rohmer, L. A. Oro, M. A. Ciriano, M. Bénard, *Inorg. Chem.* **2005**, *44*, 6536–6544; b) C. Tejel, M. A. Ciriano, B. E. Villarroya, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2003**, *115*, 547–550; *Angew. Chem. Int. Ed.* **2003**, *42*, 530–532; c) C. Tejel, M. A. Ciriano, B. E. Villarroya, R. Gelpi, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **2001**, *113*, 4208–4210; *Angew. Chem. Int. Ed.* **2001**, *40*, 4084–4086; d) F. P. Pruchnik, P. Jakimowicz, Z. Ciunik, K. Stanislawek, L. A. Oro, C. Tejel, M. A. Ciriano, *Inorg. Chem. Commun.* **2001**, *4*, 19–22; e) C. Tejel, M. A. Ciriano, J. A. López, F. J. Lahoz, L. A. Oro, *Angew. Chem.* **1998**, *110*, 1647–1650; *Angew. Chem. Int. Ed.* **1998**, *37*, 1542–1545; f) M. A. Ciriano, S. Sebastián, L. A. Oro, A. Tiripicchio, M. Tiripicchio-Camellini, *Angew. Chem.* **1988**, *100*, 406–407; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 402–403.
- [15] CCDC 867660 {[2](PF₆)₂} and 867661 {[3](PF₆)₂}, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [2](PF₆)₂: primed atoms are related to the unprimed ones by the symmetry transformation –x, –y and –z; selected bond lengths [Å] and angles [°]: Ir1–Ir2, 2.6966(8); Ir2–Ir2', 2.7772(10); Ir1–N5, 2.246(10); N5–Ir1–Ir2, 172.9(2); Ir1–Ir2–Ir2', 168.03(3); [3](PF₆)₂: selected bond lengths [Å] and angles [°]: Ir1–Ir2, 2.6923(7); Ir2–Ir3, 2.7621(6); Ir3–Ir4, 2.7935(7); Ir1–C29, 2.077(12); C29–C30, 1.223(18); C30–C31, 1.416(18); C29–Ir1–Ir2, 174.2(4); Ir1–Ir2–Ir3, 167.43(2); Ir2–Ir3–Ir4, 161.79(2).
- [16] a) M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247–422; b) B. S. Brunshwig, C. Creutz, N. Sutin, *Chem. Soc. Rev.* **2002**, *31*, 168–184.
- [17] For a review on the DOSY method, see P. S. Pregosin, P. G. A. Kumar, I. Fernández, *Chem. Rev.* **2005**, *105*, 2977–2998.
- [18] Repeated attempts to grow up monocrystals of complex [4]²⁺ using several counterions were unsuccessful. This complex is stable enough in solution to register the ¹H and ¹³C spectra, but under prolonged time in solution (about a week) the color of the solution changes slowly from purple to blue. At this point, the octanuclear species no longer exists in solution, since the ¹H NMR spectrum corresponds to the blue hexanuclear chain [{Ir₂(μ-OPy)₂(CO)₄}]₃²⁺. This disproportionation reaction is accompanied with the formation of a black insoluble material, which probably is a polymer of composition [{Ir₂(μ-OPy)₂(CO)₄}]_nC≡CPhC≡C]_n.

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Entry for the Table of Contents

Layout 2:

Catch Phrase

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Miguel A. Ciriano, and Cristina
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Connecting C≡C Bonds to Tetrairidium Chains

Tetrametallic iridium chains with the metal atoms in an average oxidation state of 1.5 and bound by unsupported metal-metal bonds have been effectively connected to organic fragments with delocalized π -electrons such as 1,4-diethynylbenzene (see Figure).

This connection allows an electronic communication along the whole chain spanning around 30 Å and sheds light on the possible use of this type of molecules as ‘molecular wires’.