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Facile synthesis of new fullerene–Ru(bpy)$_3$ dyads bearing phosphonate groups for hybrid organic–inorganic materials

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Abstract—Fullerene reacted with mono- and diphosphonate-bearing bipyridines by way of Bingel-type reactions to give adducts which were easily transformed in the corresponding dyads by forming Ru(bpy)$_3$ complexes. Electrochemical measurements and the observation of heavy quenching of the Ru(bpy)$_3$ luminescence manifested strong interactions between the active moieties. Attempts to include the dyads into inorganic matrices derived from zirconium phosphate are reported.

The conversion of solar light into useful chemical energy is a goal that in principle may artificially be achieved by the rational design of the appropriate arrangement of components in the solid state. Nevertheless, even though the preparation of solid structures is more and more in the side of designing and predictive principles conceptually similar to those used in solution chemistry,[1] we are still far from this accomplishment. However, the use of layered inorganic salts in which organic structures (i.e., electron-donor and acceptor systems) can be orderly deposited either by weak interactions or covalent bonds, a widespread technique to prepare tailored solids with coveted properties,[2] may be applied to approaching this end. Our recent work in the chemistry of metal phosphonates[3] thus prompted us to prepare, and hereby describe, dyad systems **1** and **2** (Fig. 1),[4] with the aim that their PO$_3$ groups could be appropriate anchoring points to the suitable inorganic matrix. In this way the charge-transfer process would probably benefit of a polar, solid and rigid environment, conditions that seem to be paramount in the achievement of long-lived charge-separated states.

Scheme 1 depicts the straightforward synthetic route used to prepare dyad **1**.

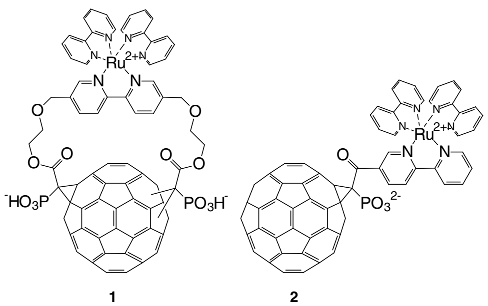

Figure 1. Dyads goal of this work.

Bromination of 5,5′-dimethyl-2,2′-bipyridine with NBS under usual conditions rendered the corresponding dibromide whose halogen atoms were easily replaced by ethyleneglycol to give diol **6**. The hydroxyl groups reacted with chlorocarbonylmethyl diethyl phosphonate, generated in situ from its carboxymethyl homologue and SOCl$_2$, yielding diphosphonate **5** ready for the double Bingel-type reaction with C$_{60}$.[5] As expected, it rendered a complex mixture as shown by NMR spectra. However, the MALDI-TOF spectrum of the reaction crude displayed an intense peak at $m/z = 1377$ amu, corresponding to $M^+ + 1$ of the mixture of the various regioisomers of **4**, together with five much less intense peaks at $m/z = 1961$, 2097, 2617, 2754 and 3474 amu. This peak occurrence may be explained as in Figure 2. It may be seen that the structures that can be assigned to the

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Keywords: Dyads; Fullerene; Ruthenium complexes; Charge transfer.
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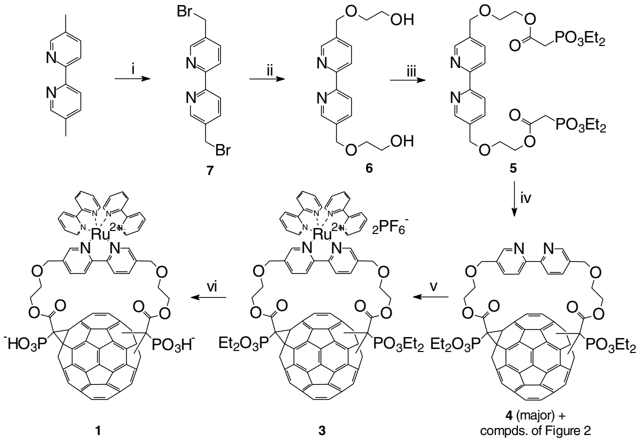


Scheme 1. Reagents and conditions: (i) NBS/CCl_4/benzoyl peroxide, 80 °C, 2 h (33%); (ii) Na/ethyleneglycol, rt 12 h (38%); (iii) carboxymethyl diethyl phosphonate/Cl_2SO/Py/CH_2Cl_2, 0–25 °C, 12 h (96%); (iv) C_{60}/toluene/DBU/I_2, rt 2 h (14%); (v) $Ru(bpy)_2Cl_2$/EtOH–H_2O/NH_4PF_6, reflux, 3 h (20%); (vi) HCl/H_2O, reflux (61%). Compound **1** was obtained as a mixture of regioisomers (see text).

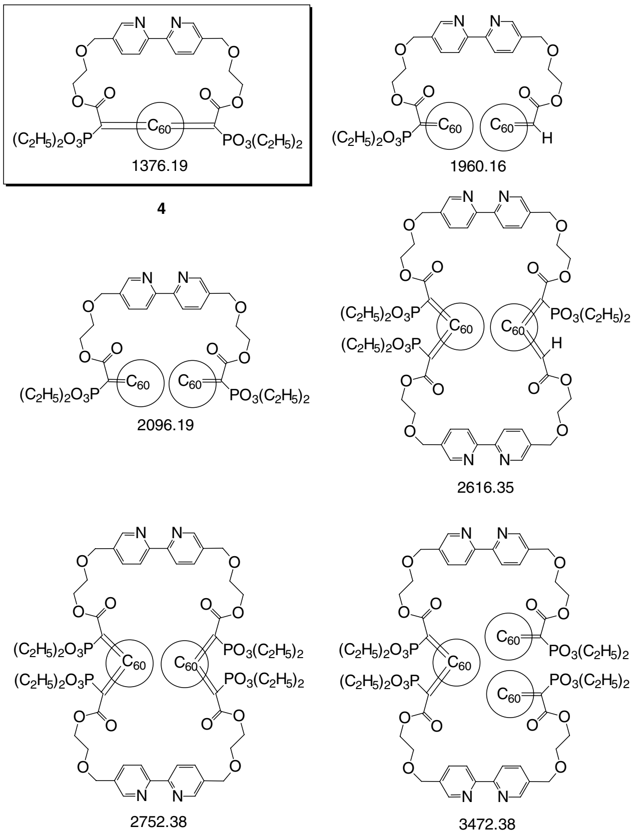


Figure 2. Proposed structure and molecular weights of the main products of the Bingel-type reaction between **5** and C_{60} (Scheme 1).

observed m/z values correspond to the reaction of two or three C_{60} units, unfavourable on entropy grounds.

Fortunately, flash chromatography over silica-gel allowed separation in 14% yield of a fraction whose MALDI-TOF spectrum only contained traces of the peaks above $m/z = 1377$. The ^1H NMR spectrum regrettably showed a very complex set of signals in the range of 7.5–8.7 ppm thus suggesting that the reaction was poorly regioselective, in contrast to what has been reported in similar situations where a tethering approach has been used to multi-functionalize fullerenes in a quite regioselective fashion.[6] Despite this outcome, we carried on because we thought a fixed regiochemistry was not essential to fulfil the goal of including the dyad into the inorganic matrix. Figure 3 contains the resulting molecular model of an idealized arrangement of *trans*-4 isomer of compound **1** (Scheme 1) with the $Ru(bpy)_3$ complex on top of C_{60}.

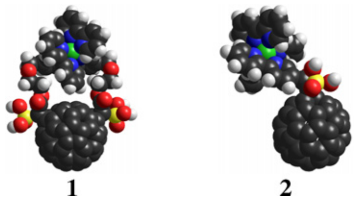
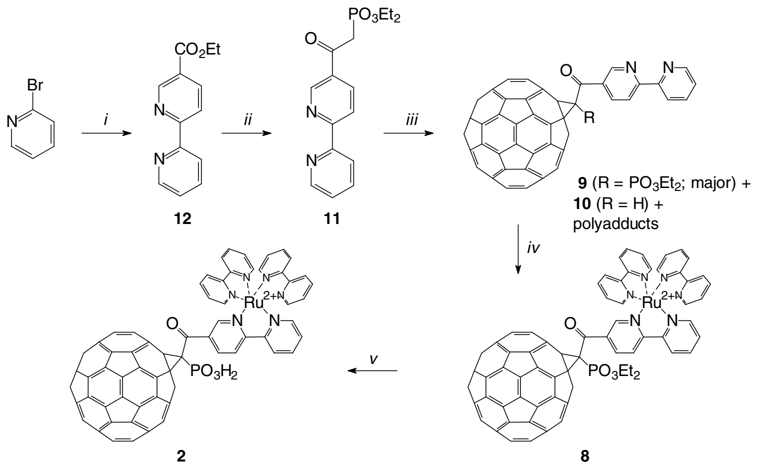


Figure 3. Calculated structures (see text) for the indicated compounds.

Dyad **1** was obtained by treatment of the mixture of isomers **4** with $Ru(bpy)_2Cl_2$ to give tetraethyl diphosphonate **3**[7] which was finally hydrolyzed in acidic media. The MALDI-TOF spectrum of **3** showed three important peaks at $m/z = 895$ (doubly charged M^{2+}), 1790 (M^+) and 1935 ($M^+ + PF_6$), while that of **1** displayed the expected one at $m/z = 1679$.

Dyad **2** was prepared according to Scheme 2. We started by Negishi coupling[8] of 2-bromopyridine with ethyl 6-chloronicotinate to render ester **12** whose condensation with the anion of diethyl methylphosphonate yielded ketophosphonate **11**.[9] Its Bingel-type reaction with C_{60} led to a complex mixture from which monoadduct **9** dominated ($m/z = 1053$) as shown by the MALDI-TOF spectrum. Flash-chromatography allowed the isolation of **9**[10] and its dephosphorylated counterpart **10**[11] in 53% and 8% yield, respectively. Compound **9** was easily transformed into the Ru complex **8**[12] and the phosphonate hydrolyzed to give dyad **2** following similar procedures as those described above.

The electrochemical profiles of dyads **1** and **2** in solution were quite complex as expected because one might anticipate a reduction pattern involving up to twelve negative potentials, half of them belonging to fullerene and the other half to Ru complex. Figure 4a and b display the reduction patterns of dyads **1** and **2**, respectively, together with the corresponding model compounds **4** and **9** for the C_{60} moiety and the complexes Ru(**5**)$(bpy)_2$ and Ru(**11**)$(bpy)_2$ prepared ad hoc by us for this study. The reduction profile of dyad **1** resembles that of **4**, its C_{60} parent, since the expected Ru complex potentials were not clearly discerned. In contrast, Ru complex of dyad **2** was reduced in an almost identical profile as that of its Ru(**11**)$(bpy)_2$ counterpart. Reduction of C_{60} of dyad **2** occurred at much less negative potentials (−0.58 and −0.96 V) as compared to its C_{60} precursor **9** (−0.80 and −1.26 V), indicating that the C_{60} reduction



Scheme 2. Reagents and conditions: (i) ethyl 6-chloronicotinate/*t*-BuLi/THF, −78 °C/$ZnCl_2$, rt/Pd(dba)$_3$·$CHCl_3$/*t*-BuP/THF, reflux (50%); (ii) $CH_3PO_3Et_2$/BuLi/THF, −78 °C, 12 h (86%); (iii) C_{60}/toluene/DBU/I_2, rt 2 h (53%); (iv) Ru(bpy)$_2Cl_2$/EtOH–H_2O/NH_4PF_6, reflux, 3 h (72%); (vi) HCl/H_2O, reflux (83%).

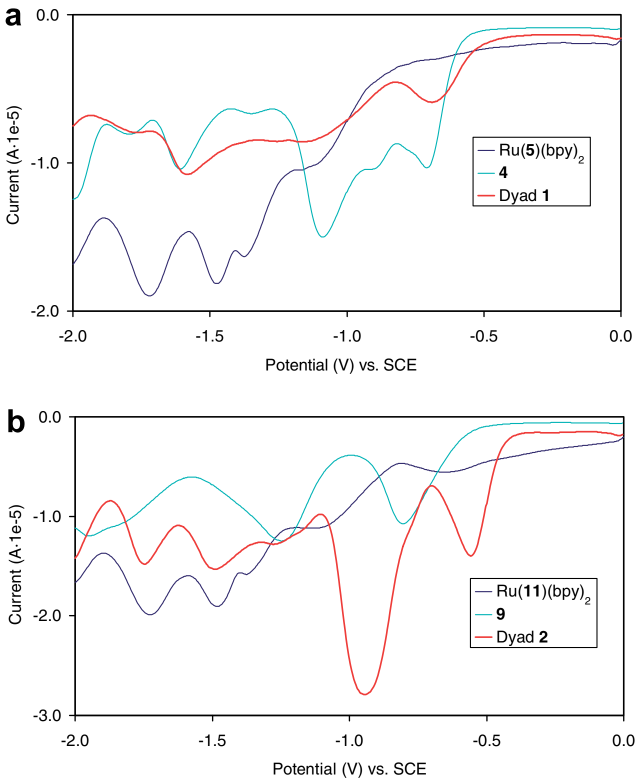


Figure 4. Current–potential responses obtained from square wave voltammetry (SWV) of the dyads **1** (a) and **2** (b) and reference compounds in dichloromethane with 0.1 M Bu_4NPF_6 as supporting electrolyte, scan rate = 0.1 V s^{-1} and glassy carbon at working electrode.

in dyad **2** was greatly facilitated by the neighbouring Ru complex as it was previously observed.[13] These findings show the strong mutual influence of the acceptor and donor moieties in dyads **1** and **2**. Reversible Ru(II) to Ru(III) oxidation (not shown in Fig. 4) was relatively uneventful because it occurred at similar values (**1**: 1.29 V; **2**: 1.40 V) as those of the reference compounds (Ru(**5**)(bpy)$_2$: 1.28 V; Ru(**11**)(bpy)$_2$: 1.43 V).

Observation of Figure 5 shows that the UV–vis spectra of dyads **1** and **2** were the simple addition of those of their individual components within experimental error.

Luminescence measurements revealed again the intense interaction between fullerene and Ru complex in the dyads. It may easily be seen in Table 1 that the quantum yields of Ru emission were strongly reduced in dyads **1** and **2**. Whether this emission quench is: (i) the consequence of the promoted electron being passed to fullerene thus creating a charge-separated state and heavily reducing the probability of direct, radiative deactivation of the metal complex; or (ii) the effect of energy transfer to the low lying triplet excited-state of C_{60} remains to be seen until further experiments are performed. The fact that increasing solvent polarity further decreased ϕ seems to point to charge separation because this is to be stabilized in the more polar solvent. In any case, the interaction between C_{60} and Ru(bpy)$_3$ appeared to be: (i) more effective in dyad **1** as suggested by the highest diminution of ϕ (ca. 99% regardless of solvent) relative to its reference compound; (ii) more sensitive to solvent polarity in dyad **2** because ϕ was further reduced in CH_3CN (91%) as compared to the less polar CH_2Cl_2 (71%). These observations may be the consequence of the structural differences between the studied dyads, stiffer **1** displaying a better performance.

Unfortunately, all attempts of slipping dyads **1** and **2** within the walls of zirconium phosphate were

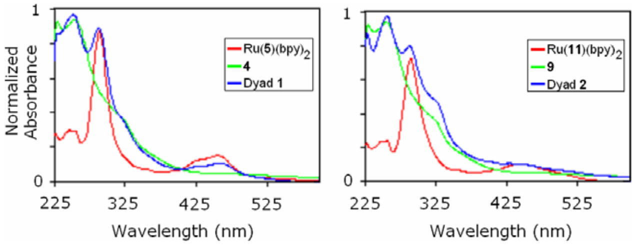


Figure 5. UV–vis absorption spectra of dyads **1**, **2** and reference compounds (10^{-5} M in dichloromethane).

Table 1. Luminescence data of dyads **1**, **2** and reference compounds in aerated solutions

Compound[a] (solvent)	λ_{exc} (nm)	λ_{ems} (nm)	Emission intensity	ϕ (10^{-4})
Ru(**5**)(bpy)$_2$ (a)	455	606	996	12.54
(b)	457	617	283	4.51
Ru(**11**)(bpy)$_2$ (a)	447	618	220	3.62
(b)	442	619	77	2.24
Dyad **1** (a)	455	606	8	0.09
(b)	457	616	3	0.03
Dyad **2** (a)	447	601	19	0.83
(b)	442	612	10	0.21

[a] $c = 10^{-5}$ M; $a = CH_2Cl_2$; $b = CH_3CN$.

unsuccessful using the typical exfoliating methods (1:1 water/acetone suspension at 80 °C and alkylamine intercalation)[3]. In the case of dyad **2**, we tried an alternative method[14] by means of its treatment with Zr(n-BuO)$_4$ in n-BuOH. In this way we obtained an amorphous solid (it gave no discernible powder X-ray pattern), whose elemental analyses by combustion and ICP-MS[15] were compatible with the approximate molecular formula Zr(**2**)$_{0.2–0.4}$(n-BuO)$_{3.6–3.8}$ what suggests that the dyad was in fact integrated in the inorganic matrix. Solid-state MAS 'non-CP' ^{31}P NMR spectra (Fig. 6a) showed the phosphonate signals slightly shielded (12 ppm) relative to the starting dyad whose multiplet at −144.7 belonging to the PF$_6$ counterions is hardly visible in the Zr derivative, indicating that Ru(II) charge compensation is no longer performed by these anions. Solid-state CP MAS ^{13}C NMR spectra (Fig. 6b) revealed the aliphatic carbons of the butoxide. Thermogravimetric analysis indicated that the solid is stable at temperatures below ca. 300 °C. Above this mark, a heavy 80% loss was attained in a relatively narrow temperature range (>200 °C) where all carbon content was lost.

Last but not least, we observed that the organic–inorganic assembly resulted negligible luminescent in the solid state (λ_{exc} = 455 nm) what suggests that the strong interaction between the active moieties observed in solution prevailed in the solid state. Further studies are under way to include these dyads into crystalline inorganic matrices.

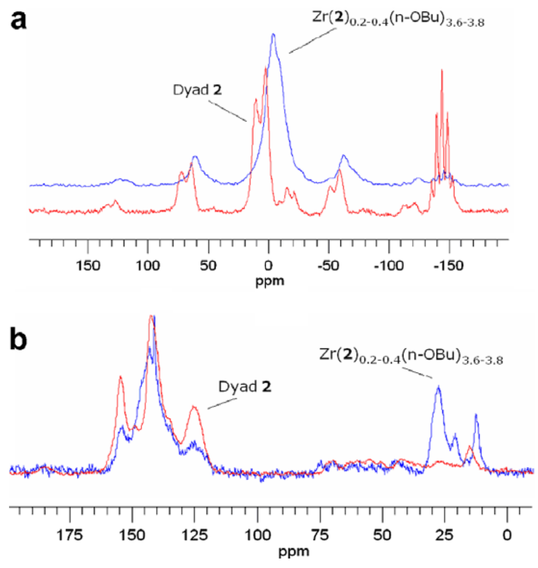


Figure 6. Solid-state NMR spectra ((a) MAS, 'non-CP' ^{31}P; (b) CP-MAS ^{13}C) of dyad **2** and the compound resulting from its reaction with Zr(On-Bu)$_4$.

Acknowledgements

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References and notes

1. Desiraju, G. R. In *Stimulating Concepts in Chemistry*; Wiley-VCH, 2000; pp 293–306; Dey, A.; Kirchner, M. T.; Vangala, V. R.; Desiraju, G. R.; Mondal, R.; Howard, J. A. K. *J. Am. Chem. Soc.* **2005**, *127*, 10545.
2. Kumar, C. V.; Raju, B. B. *Mol. Supramol. Photochem.* **2001**, *8*, 505; Mitzi, D. B. *Chem. Mater.* **2001**, *13*, 3283; Pergher, S. B. C.; Corma, A.; Fornes, V. *Quim. Nova* **1999**, *22*, 693; Byrd, H.; Suponeva, E. P.; Andrew, B.; Bocarsly, A. B.; Thompson, M. E. *Nature* **1996**, *380*, 610.
3. Brunet, E.; Huelva, M.; Vázquez, R.; Juanes, O.; Rodríguez-Ubis, J. C. *Chem. Eur. J.* **1996**, *12*, 1578; Brunet, E.; de la Mata, M. J.; Juanes, O.; Rodriguez-Ubis, J. C. *Chem. Mater.* **2004**, *16*, 1517; Brunet, E.; de la Mata, M. J.; Juanes, O.; Rodriguez-Ubis, J. C. *Angew. Chem., Int. Ed.* **2004**, *43*, 619–621; Brunet, E. *Chirality* **2002**, *14*, 135; Brunet, E.; Alhendawi, H. M. H.; Cerro, C.; de la Mata, M. J.; Juanes, O.; Rodríguez-Ubis, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 6918; Brunet, E.; Alonso, M.; de la Mata, M. J.; Fernandez, S.; Juanes, O.; Chavanes, O.; Rodriguez-Ubis, J. C. *Chem. Mater.* **2003**, *15*, 1232.
4. For recent examples of several dyad systems see: Modin, J.; Johanson, H.; Grennberg, H. *Org. Lett.* **2005**, *7*, 3977; Cardinali, F.; Gallan, J.-L.; Schergna, S.; Maggini, M.; Nierengarten, J.-F. *Tetrahedron Lett.* **2005**, *46*, 2969; Chaignon, F.; Torroba, J.; Blart, E.; Borgströn, M.; Hammarströn, G.; Odobel, F. *New J. Chem.* **2005**, *29*, 1272; Clifford, J. N.; Accorsi, G.; Cardinali, F.; Nierengarten, J.-F.; Armaroli, N. *C.R. Chimie* **2006**, *9*, 1005; Zhou, Z.; Sarova, G. H.; Zhang, S.; Ou, Z.; Tat, F. T.; Kadish, K. M.; Echegoyen, L.; Guldi, D. M.; Schuster, D. I.; Wilson, S. R. *Chem. Eur. J.* **2006**, *12*, 4241.
5. Spectroscopic data of **5** (mp 46 °C): ^{1}H NMR (CDCl$_3$, 300 MHz) δ: 1.18 (t, 12H, J = 6.9 Hz, 4 × CH$_3$); 2.89 (d, 4H, $J_{H–P}$ = 21.5 Hz, 2 × CH$_2$P); 3.63 (t, 4H, J = 4.8 Hz,

$2\times CH_2$); 4.04 (m, 8H, $4\times CH_2$); 4.23 (t, 4H, $J=4.8$ Hz, $2\times CH_2$); 4.51 (s, 4H, $2\times CH_2$); 7.67 (dd, 2H, $J_{4-3}=8.1$ Hz, $J_{4-6}=2.1$ Hz, H_4); 8.25 (d, 2H, $J_{3-4}=8.1$ Hz, H_3); 8.50 (d, 2H, $J_{6-4}=2.1$ Hz, H_6). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 16.1 (CH_3); 33.4 (d, $J_{C\text{–}P}=114.7$ Hz, CH_2P); 62.4 (CH_2); 64.1; 67.8; 70.2 ($3CH_2$); 120.4 (C_3); 133.1 (C_5); 136.0 (C_4); 148.2 (C_6); 155.1 (C_2); 165.4 (CO). MS. (L-SIMS+): 661.2 ($M+H^+$, 100); 683.2 ($M+Na^+$, 21).

6. See, for example, Reuther, U.; Brandmüller, T.; Donaubauer, W.; Hampel, F.; Hirsch, A. *Chem. Eur. J.* **2002**, *8*, 2261.
7. Its ^1H NMR ($CDCl_3$, 300 MHz) was very complex but the following groups of signals could be discerned at δ: 1.47 (12H, $4\times CH_3$); 4.01 (4H, $2\times CH_2$); 4.54 (m, 12H, $4\times CH_2$, $2\times CH_2$); 4.64 (m, 4H, $2\times CH_2$); 7.67–8.98 (m, 22H).
8. Lützen, A.; Hapke, M. *Eur. J. Org. Chem.* **2002**, 2292.
9. Spectroscopic data of **11**: ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.42 (t, 6H, $J=7.1$ Hz, $2\times CH_3$); 3.82 (d, 2H, $J_{H\text{–}P}=22.1$ Hz, CH_2); 4.30 (m, 4H, $2\times CH_2$); 7.51 (ddd, 1 H, $J_{5'-3'}=1.1$ Hz, $J_{5'-4'}=9.6$ Hz, $J_{5'-6'}=5.0$ Hz, $H_{5'}$); 7.98 (ddd, 1H, $J_{4'-3'}=7.9$ Hz, $J_{4'-6'}=2.1$ Hz $H_{4'}$); 8.52 (m, 1H); 8.59 (m, 1H); 8.86 (d, 1H, $J=4.2$ Hz); 9.41 (d, 1H, $J_{6-5}=1.5$ Hz, H_6). ^{13}C-RMN ($CDCl_3$, 75 MHz) δ: 16.1 (CH_3); 38.7 (d, $J_{C\text{–}P}=128.4$ Hz, CH_2P); 62.5 (OCH_2); 119.4 ($C_{3'}$); 122.4 (C_3); 123.4 ($C_{5'}$); 134.1 (C_5); 136.8 ($C_{4'}$); 137.0 (C_4); 148.9 (C_6); 149.8 ($C_{6'}$); 154.5 (C_2); 159.4 ($C_{2'}$); 190.4 (d, $J_{C\text{–}P}=6.3$ Hz, CO). MS (MALDI-TOF): 335.1 ($M+H^+$).
10. Spectroscopic data of **9**: ^1H NMR ($CDCl_3$, 300 MHz) δ: 1.17 (t, 6H, $J=7.1$ Hz, $2\times CH_3$); 4.40 (m, 4H, $2\times CH_2$); 7.39 (ddd, 1H, $J_{5'-3'}=1.2$ Hz, $J_{5'-4'}=9.7$ Hz, $J_{5'-6'}=5.0$ Hz, $H_{5'}$); 7.87 (ddd, 1H, $J_{4'-3'}=7.9$ Hz, $J_{4'-6'}=2.1$ Hz $H_{4'}$); 8.54 (d, 1H, $H_{3'}$); 8.66 (d, 1H, $J_{3\text{–}4}=8.5$ Hz, H_3); 8.74 (dd, 1H, $H_{6'}$); 8.96 (dd, 1H, $J_{4-6}=2.3$ Hz, H_4); 9.91 (d, 1H, H_6). ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 16.3 (d, $J_{C\text{–}P}=6.3$ Hz, CH_3); 22.1 (d, $J_{C\text{–}P}=117.9$ Hz, C); 64.6 (d, $J_{C\text{–}P}=8.4$ Hz, CH_2); 120.8 ($C_{3'}$); 122.4 (C_3); 124.8 ($C_{5'}$); 130.0; 136.9 (C_5); 137.1 ($C_{4'}$); 138.4 (C_4); 141.0; 141.9; 142.1; 142.7; 142.9; 143.0; 143.1; 144.0; 144.5; 144.6; 144.7; 144.9; 145.0; 145.2; 145.3; 149.5 (C_6); 151.4 ($C_{6'}$); 154.8 (C_2); 160.1 ($C_{2'}$); 186.9 (CO). MS (MALDI-TOF): 1053.2 (M^+).
11. Spectroscopic data of **10**: ^1H NMR ($CDCl_3$, 300 MHz) δ: 6.69 (s, 1H, CH); 7.47 (m, 1H); 7.89 (m, 1H); 8.52 (m, 1H); 8.59 (m, 1H); 8.78 (d, 1H, $J=4.2$ Hz); 9.41 (d, 1H, $J=1.5$ Hz). MS (MALDI-TOF): 917.2 (M^+).
12. Spectroscopic data of **8**: ^1H NMR (acetone-d_6, 300 MHz) δ: 1.39 (t, 6H, $J=7.1$ Hz, $2\times CH_3$); 4.42 (m, 4H, $2\times CH_2$); 7.58 (m, 3H); 7.65 (m, 2H); 8.19 (m, 11H); 8.77 (m, 4H); 8.99 (m, 1H); 9.11 (m, 2H). ^{13}C NMR (acetone-d_6, 75 MHz) δ: 16.5 (d, $J_{C\text{–}P}=6.3$ Hz, CH_3); 20.0 (d, $J_{C\text{–}P}=95.8$ Hz, C); 65.8 (d, $J_{C\text{–}P}=6.3$ Hz, OCH_2); 124.6; 124.8; 124.9; 125.1; 125.4; 126.8; 128.3; 128.4; 128.5; 128.6; 129.5; 137.1; 137.1; 138.4; 138.7; 138.8; 141.3; 141.4; 141.9; 142.5; 143.0; 143.4; 143.5; 143.6; 144.3; 144.6; 145.0; 145.1; 145.4; 145.6; 145.6; 149.7; 151.6; 151.7; 152.3; 156.1; 157.0; 157.2; 157.4; 161.5; 184.5 (CO). MS (MALDI-TOF): 734.0 (M^{2+}); 1466.0 (M^+); 1611.0 [$(M+PF_6)^+$].
13. Rio, Y.; Enderlin, G.; Bourgogne, C.; Nierengarten, J.-F.; Gisselbrecht, J.-P.; Gross, M.; Accorsi, G.; Armaroli, N. *Inorg. Chem.* **2003**, *42*, 8783.
14. Ngo, H. L.; Hu, A.; Lin, W. *J. Mol. Catal. A: Chem.* **2004**, *215*, 177.
15. Elemental analysis found: 66.2 C, 3.3 H, 3.5 N. ICP-MS: Zr (100 u.m.a.), Ru (23.7 u.m.a.), P (16.5 u.m.a.).