Synthesis and coordinative properties of a hybrid bis(diphenylphosphino)methane–terpyridine

Guillaume Pickaert,[a] Michèle Cesario,[b] Laurent Douce[a] and Raymond Ziessel*[a]

[a] *Laboratoire de Chimie, d'Electronique et Photonique Moléculaires, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur, 25 rue Becquerel, F-67087 Strasbourg Cedex 02, France. E-mail: ziessel@chimie.u-strasbg.fr*

[b] *Institut de Chimie des Substances Naturelles, CNRS, F-91128 Gif-sur-Yvette, France*

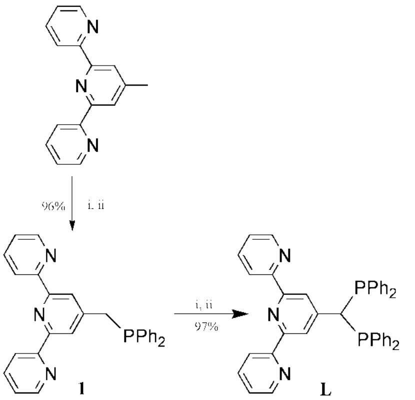
Received (in Cambridge, UK) 31st March 2000, Accepted 15th May 2000

A newly-synthesized 4′-[bis(diphenylphosphino)methane]–2,2′:6′,2″-terpyridine-based (dppm–terpy) ligand forms complexes by selective complexation of the terpy or diphos segment, respectively, with Fe(II) or Pd(II) salts; in the latter case, an X-ray structural analysis reveals the formation of a neutral square-planar complex assembled from the deprotonated ligands.

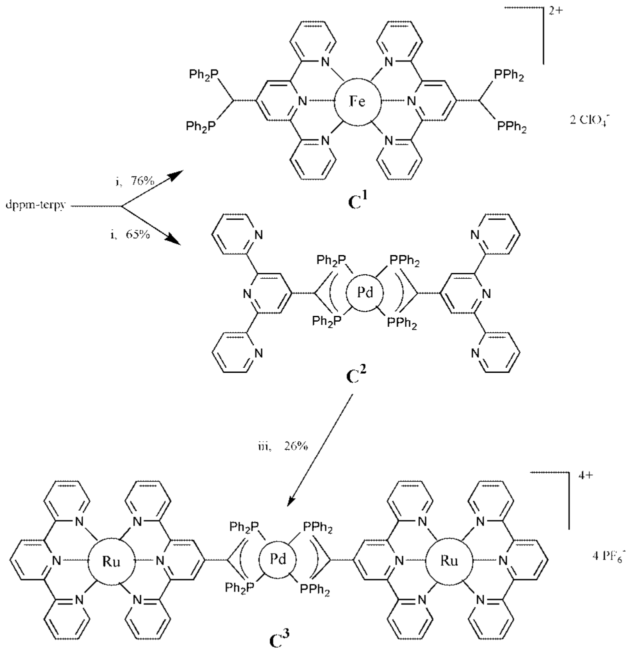
The 2,2′:6′,2″-terpyridine (terpy) molecule is widely used in transition metal chemistry as a meridionally coordinating and tridentate chelating ligand. Multiple applications have been found in the areas of analysis and the design of molecular electronic devices.[1] Phosphine-functionalized terpy entities, such as terpyPPh$_2$[2] and terpyPO$_3$H$_2$,[3] readily complex many different transition metals and bind strongly to certain semiconductors. We have shown recently that terpyCH$_2$P(O)Ph$_2$ can be deprotonated under mild conditions to produce a useful synthon for the preparation of carotenoid-based photoactive molecular-scale wires.[4] In light of the rich coordination chemistry of bis(diphenylphosphino)methane (dppm), a species well known in organometallic chemistry as a monodentate, bidentate or bridging ligand,[5] it was anticipated that the hitherto unreported terpy analogue (dppm–terpy) might be a valuable building block for the construction of multimetallic networks. Interest in such polynuclear assemblies is stimulated by the study of intramolecular electron or energy transfer processes[6] as well as by the coupling of luminophoric metal centers to photoactive catalytic sites.

We present here, the synthesis and coordination behaviour of a hybrid diphos/terpy ligand where the complexation behaviour is governed by the choice of the metal precursor. Ligand **L** is prepared in a stepwise fashion from the deprotonated mono-phosphine-terpy ligand **1**, followed by nucleophilic substitution with PPh$_2$Cl as illustrated in Scheme 1. The dppm–terpy ligand **L** is characterized by a ^{31}P NMR signal at δ −3.7 (singlet), compared to intermediate **1** which gives a singlet at δ −8.5. The corresponding phosphine oxide **L(O)$_2$**, obtained under phase transfer conditions with NaIO$_4$ as oxidant, shows a ^{31}P NMR signal at δ 29.5, with the CH proton appearing as a triplet at δ = 5.00, J_{HP} 14.4 Hz. A strong IR absorption band is found at 1210 cm^{-1} ($\nu_{P=O}$).

The ambivalent reactivity of dppm–terpy is demonstrated by virtue of its interaction with Fe and Pd precursors. Thus, reaction of **L** with Fe(ClO$_4$)$_2$·6H$_2$O gives a deep-violet complex whose structure is assigned as **C^1**.† Both the intense MLCT absorption band centred at 562 nm (ε = 20450 dm^3 mol^{-1} cm^{-1}) and the slightly shifted singlet observed (δ 3.2 in CDCl$_3$) in the ^{31}P NMR spectrum are indicative of complexation at the terpy segment. Note that the related Fe(II) complex formed from **L(O)$_2$** gives a singlet at δ 30.0 (CD$_3$CN). In contrast, ligand **L** reacts with [Pd(acac)$_2$] (acac = acetylacetonate) to form a sparingly soluble, deep-yellow compound (λ_{max} = 407 nm, ε = 43450 dm^3 mol^{-1} cm^{-1}) that lacks the signal characteristic of the CH fragment in the proton NMR spectrum but displays a ^{31}P NMR signal at δ −29.9 (singlet in CD$_2$Cl$_2$). The presence of uncomplexed terpy fragments within this latter complex, labelled as **C^2** in Scheme 2, was confirmed by an X-ray diffraction study (*vide infra*). The dppm–terpy ligands are deprotonated during the process so that the overall product is a neutral palladium(II) complex. It is likely that the acac anion operates as a buffer to deprotonate the ligand.[7]



Scheme 1 *Reagents and conditions*: i, Bu^{n}Li, Pr$^i{}_2$NH, THF, −78 °C; ii, Ph$_2$PCl, THF.



Scheme 2 *Reagents and conditions*: i, Fe(ClO$_4$)$_2$·6H$_2$O, methanol–dichloromethane; ii, [Pd(acac)$_2$], THF; iii, [Ru(terpy)(dmso)Cl$_2$], methanol, AgBF$_4$, 80 °C; all reactions were carried out using argon degassed solutions.

DOI: 10.1039/b002586k

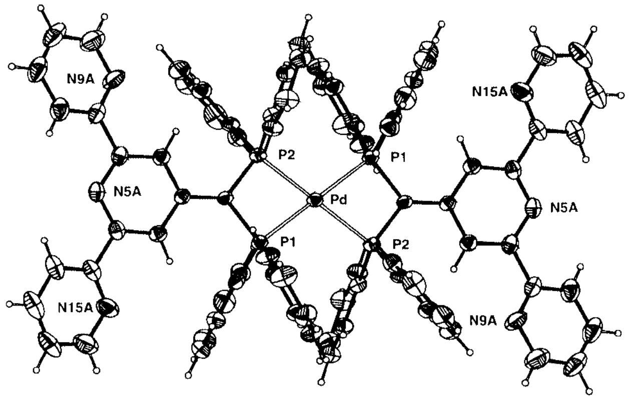


Fig. 1 ORTEP drawing of complex $\mathbf{C}^2$ (Displacement ellipsoids are shown at the 50% probability level); Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Pd–P(1) 2.317(2), Pd–P(2) 2.315(2), P(1)–C(terpy) 1.756(4), P(1)–C(phenyl) 1.826(5), P(1)–C(phenyl) 1.822(5), P(2)–C(terpy) 1.764(4), P(2)–C(phenyl) 1.818(4), P(2)–C(phenyl) 1.823(5), P(2)*–Pd–P(2) 180.0, P(2)–Pd–P(1)* 109.09(5), P(2)–Pd–P(1) 70.91(5), P(1)–C(terpy)–P(2) 99.5(2).

The single-crystal X-ray analysis‡ (Fig. 1) indicates that the palladium atom is in a square-planar environment with the four P atoms coordinated to the metal centre and with two uncoordinated terpyridines. The crystals consist of discrete neutral centrosymmetric molecules, the Pd atom being located on an inversion centre. As expected, all six N-atoms are in a transoidal arrangment that minimizes electronic interactions.[8] An angle of 16.0(0)° between the planes defined by the two pyridine rings containing N(5A) and N(15A) and a dihedral angle of 16.8(0)° between the planes of the external rings containing N(15A) and N(9A) illustrate twisting about the interannular C–C bonds, as well as the slight distortion within the terpy subunit. Owing to the anionic nature of the coordinated diphos–terpy ligands the C–P bond distances (*ca.* 1.76 Å) are shorter than in related Pd(II)-phosphine complexes.[9] The bite angle P(1)–Pd–P(2) of 70.91(5)° and the twist of the phenyl rings around the P atom *versus* the plane defined by the square containing the palladium (71–75°) are in good agreement with values expected for a regular square-planar coordination polyhedron.

This mononuclear Pd(II) complex is of interest as a potential *metallo-synthon* for the construction of more elaborate molecular architectures in which the electronic interaction between both sites could, in principle, be tuned by the oxidation state of the central metal. In order to demonstrate this principle, we chose to complex the free terpy moieties with [Ru(terpy)(dmso)Cl_2][10] under mild conditions. The heterotrinuclear complex $\mathbf{C}^3$ has a characteristic MLCT absoption band at 482 nm (ε = 43000 $dm^3\ mol^{-1}\ cm^{-1}$), and exhibits a singlet in the ^{31}P NMR spectra at δ −10.6 (CD_3CN). The MALDI-TOF mass spectra is in keeping with the proposed structure.†

The redox behaviour of these complexes was studied by cyclic voltammetry in MeCN (for $\mathbf{C}^1$ and $\mathbf{C}^3$) or dichloromethane (for $\mathbf{C}^2$) containing $NBu^n{}_4PF_6$ (0.1 mol dm^{-3}) as supporting electrolyte. The Pd(II) complex $\mathbf{C}^2$ exhibits two irreversible oxidation waves at $E_{pa}(1) = 0.69$ and $E_{pa}(2) = 1.04$ V *vs.* SCE using ferrocene as internal reference (Fc/Fc$^+$ = 0.41 V). No peaks are seen upon reductive scans, at least above −2.0 V *vs.* SCE. The oxidative processes can be ascribed to the successive oxidation of the anionic terpy–diphos ligands. Within the mixed Ru/Pd complex $\mathbf{C}^3$, ligand-based oxidation steps are found at $E_{pa}(1) = 0.87$ and $E_{pa}(2) = 1.06$ V *vs* SCE. This complex also exhibits a single metal-based oxidation at 1.34 V *vs.* SCE (ΔE_p = 80 mV) and two irreversible terpy-based reductions at $E_{pc}(1) = -1.28$ V and $E_{pa}(2) = -1.49$ V. It is surmised that the unusual irreversibility of the ligand reduction is due to the strong electron density provided by the anionic Ph_2PCPPh_2 fragment appended to the terpy units. As expected, complex $\mathbf{C}^1$ exhibits three well-defined and reversible redox processes; namely, a single oxidation at 1.26 V (ΔE_p = 70 mV) and two ligand-centered reductions at −1.20 V (ΔE_p = 74 mV) and −1.39 V *vs.* SCE (ΔE_p = 66 mV). The easier Fe(II) oxidation *vs.* Ru(II) in $\mathbf{C}^3$ is in keeping with related unsubstituted terpy complexes.[11]

Preliminary steady-state emission studies show that complex $\mathbf{C}^2$, in the solid state (0.5% dispersed in $MgSO_4$), exhibits an intense but structureless emission band at 590 nm when excited at 400 nm. This emission is not observed in deoxygenated acetonitrile solution. Additional photophysical measurements will be carried out in order to explore the photoreactivity of $\mathbf{C}^3$.

In summary, we describe a simple strategy for the synthesis of hybrid ligands carrying hard and soft complexation centres. The diphos or the terpy part of the ligand can be complexed with good selectivity, using either Pd(II) or Fe(II), respectively. Further complexation of the free terpy centers with redox-active Ru(II) fragments facilitates preparation of linear heterotrinuclear complexes in a controlled manner. On-going experiments will study the chemistry of these novel multitopic systems.

Notes and references

† Synthetic details will be reported elsewhere. All new compounds gave satisfactory elemental analyses and were authenticated by ^1H and ^{13}C NMR, FTIR and MS. All ^{31}P NMR chemical shift are referenced using H_3PO_4 (85% in water) as internal standard. *Selected data*: for $\mathbf{C}^1$; FAB *m*/*z* (*m*-NBA) 1386.0 [M − ClO_4]$^+$. Found: C, 64.49, H, 4.13, N, 5.41. $C_{80}H_{62}N_6O_8P_4Cl_2Fe$ requires C, 64.66; H, 4.21; N, 5.66%. For $\mathbf{C}^2$; FAB$^+$ (*m*-NBA): *m*/*z* 1335.0 [M+H]$^+$. Found: C, 71.85, H, 4.47, N, 6.17. $C_{80}H_{60}N_6P_4Pd$ requires C, 71.94; H, 4.53; N, 6.29%. For $\mathbf{C}^3$; MALDI-TOF *m*/*z* 2439.4 [M − PF_6]$^+$, 2294.9 [M − 2PF_6]. Found: C, 51.57, H, 3.48, N, 7.53. $C_{110}H_{82}N_{12}P_8PdRu_2F_{24}.2C_2H_3N$ requires C, 51.35; H, 3.33; N, 7.35%.

‡ *Crystal data* for $\mathbf{C}^2$: $C_{80}H_{60}N_6P_4Pd$, M = 1335.62, monoclinic, space group $P2_1/n$, yellow crystals, a = 11.477(4), b = 25.327(9), c = 11.595(5) Å, β = 98.54(4)°, V = 3333(2) Å^3, Z = 2, T = 293 K, D_c = 1.331 g cm^{-3}, μ = 0.425 mm^{-1}, $F(000)$ = 1376. The final conventional R_1 factor is 0.0705 for 4185 data and 398 parameters, and 0.11 for all data, wR_2 = 0.1423 (all data), goodness of fit = 1.068; largest peak and hole in the final difference map were within +0.59 and −0.45 e Å^3. CCDC 182/1638. See http//www.rsc.org/suppdata/cc/b0/b002586k for crystallographic files in .cif format.

1 E. C. Constable, *Transition Metals in Supramolecular Chemistry*, Kluwer, Dordrecht, 1994, p. 81; R. Ziessel, *J. Chem. Educ.*, 1997, **74**, 673; R. Ziessel, *Synthesis*, 1999, 1839.
2 E. C. Constable, C. E. Housecroft, M. Neuburger, A. G. Schneider and M. Zehnder, *J. Chem. Soc., Dalton Trans.*, 1997, 2427.
3 S. M. Zakeeruddin, M. K. Nazeeruddin, P. Pechy, F. P. Rotzinger, R. Humphry-Baker, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1997, **36**, 5937.
4 G. Pickaert and R. Ziessel, *Tetrahedron Lett.*, 1998, **39**, 3497.
5 R. J. Puddephatt, *Chem. Soc. Rev.*, 1983, **12**, 99.
6 B. Whittle, N. S. Everest, C. Howard and M. D. Ward, *Inorg. Chem.*, 1995, **34**, 2025.
7 H. Hashimoyo, S. Okeya and Y. Nakamura, *Bull. Chem. Soc. Jpn.*, 1988, **61**, 1593.
8 A. Harriman, M. Hissler, R. Ziessel, A. De Cian and J. Fisher, *J. Chem. Soc., Dalton Trans.*, 1995, 4067 and references therein.
9 J. Barkley, M. Ellis, S. J. Higgins and M. K. McCart, *Organometallics*, 1998, **17**, 1725.
10 V. Grosshenny and R. Ziessel, *J. Organomet. Chem.*, 1993, **453**, 19.
11 D. E. Morris, K. W. Hanck and M. Keith DeArmond, *J. Electroanal. Chem.*, 1983, **149**, 115.