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Synthesis of 2-picolyl functionalized η5-cyclopentadienyl derivatives of rhodium(I) and iridium(I) and preliminary study of their reaction with ruthenium(II) for assembling hetero-bimetallic complexes

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Abstract

The 2-picolylcyclopentadienyl derivatives of rhodium(I) and iridium(I) of formula $[M\{\eta^5\text{-}C_5H_4(2\text{-}CH_2C_5H_4N)\}(\eta^4\text{-}C_8H_{12})]$ (**3**) (M = Rh) and (**4**) (M = Ir) are obtained in good yields by reacting 2-picolylcyclopentadienyllithium (**7**) with $[RhCl(\eta^4\text{-}C_8H_{12})]_2$ and $[IrCl(\eta^4\text{-}C_8H_{12})]_2$, respectively. The corresponding dicarbonyl derivatives, $[M\{\eta^5\text{-}C_5H_4(2\text{-}CH_2C_5H_4N)\}(CO)_2]$ (**5**) (M = Rh) and **6** (M = Ir), are obtained in good yields by reacting 2-picolylcyclopentadienylthallium(I) (**8**) with $[RhCl(CO)_2]_2$ and $[IrCl(C_5H_5N)(CO)_2]$, respectively. **5** has already been reported in the literature. The new complexes were characterized by elemental analysis, mass spectrometry, ^{1}H NMR, FT-IR, and UV–Vis (210–330 nm) spectroscopy. The UV–Vis spectra indicate the existence of some electronic interaction between the 2-picolinic chromophore and the cyclopentadienyl-metal moiety. The study of the electrochemical behaviour of **3–6** by cyclic voltammetry (CV) allows the interpretation of the electrode processes and gives information about the location of the redox sites. Moreover, various synthetic strategies were tested in order to try to coordinate the complexes **3–6** to a ruthenium(II) centre, but most of them failed. Instead, the hetero-bimetallic complex bis(2,2′-bipyridine)[(η5-2-picolylcyclopentadienyl)(η4-cycloocta-1,5-diene)rhodium(I)]chlororuthenium(II)-(hexafluorophosphate) (**13**), was obtained, although in poor yields (10%), by reacting the nitrosyl complex $[RuCl(bipy)_2(NO)][PF_6]_2$ **14** (bipy = 2,2′-bipyridine) first with potassium azide and then with the rhodium(I) complex **3**. The analogous complex bis(2,2′-bipyridine)(2-picoline)chlororuthenium(II)-(hexafluorophosphate) (**15**), that carries a ruthenium-bonded 2-picoline molecule instead of **3**, has prepared in the same way. **13** and **15** were characterized by elemental analysis, mass spectrometry, and ^{1}H NMR.
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1. Introduction

During the last years, some of us have synthesized several new coordination compounds in which a fluorophoric fragment, which behaves as an *antenna*, is connected to one, **1**, or two cyclopentadienyl-metal moieties, **2** [1]. Compounds of this type allowed to test whether and how the active sites, i.e., the 9-anthryl fluorophore and the cyclopentadienyl-metal moiety, interact with each other in those conditions (chemical, photo-physical, and electrochemical) which can induce the intramolecular transmission of electronic effects.

M = Rh or Ir

L = olefins; diolefins; CO; PPh₃
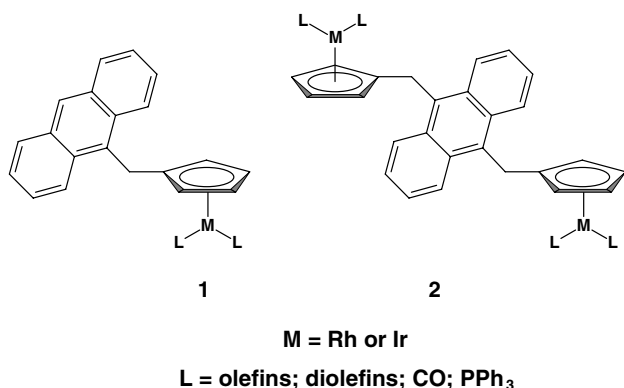
The availability of transition metal compounds which have interesting electronic, magnetic or photo-chemical properties may be relevant to design new metal-containing building blocks which could be used to obtain useful assemblies for applications in the field of molecular electronics (opto-electronics, molecular wires, switches, and molecular magnets) [2]. In this connection, another research line has now been started aimed to extend our studies to a new type of bimetallic derivatives having the following general structure:
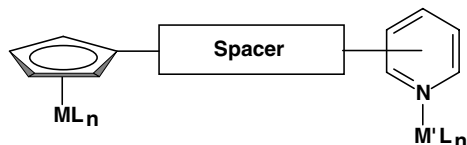

The preparation of such compounds is based on the functionalization of the Cp ligand with a pyridyl group in order to take advantage of the coordinative potentialities of the pyridinic nitrogen atom. Thus, the presence of both the cyclopentadienyl and the pyridyl ligands within the same molecular skeleton offers, at least in principle, an easy way to assemble two transition metals in the same molecular structure. By the way, it must be underlined that, from the discovery of the so-called '*pendent aminoalkyl effect*' [3], considerable interest has been focused on the cyclopentadienyl transition metal derivatives carrying a pendent nitrogen-functionalized group [4]. For this reason we have started our synthetic program focusing our attention on 2-picolylcyclopentadienyl derivatives, having in mind to extend the study to the corresponding 3- and 4-picolyl derivatives.

In the field of hetero-bimetallic complexes, the employment of a redox couple is of particular interest since donor–acceptor dyads can offer the opportunity to gain a deeper understanding of electron/energy transfer behaviour in transition metal compounds [5].

In this paper, we report the preparation, the characterization, and the study of the UV–Vis and electrochemical properties of the rhodium(I) and iridium(I) derivatives **3–6**. Complex **5** has already been described by Rausch et al. [4]. Furthermore, we devoted some

efforts to use the complexes **3–6** as ligands and succeeded in obtaining a ruthenium(II)–rhodium(I) bimetallic compound in which **3** is coordinated to a ruthenium(II) centre through its picolinic nitrogen atom, which demonstrates the potential utility of 2-picolylcyclopentadienyl ligand in the preparation of a variety of bimetallic compounds.
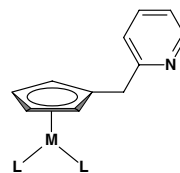
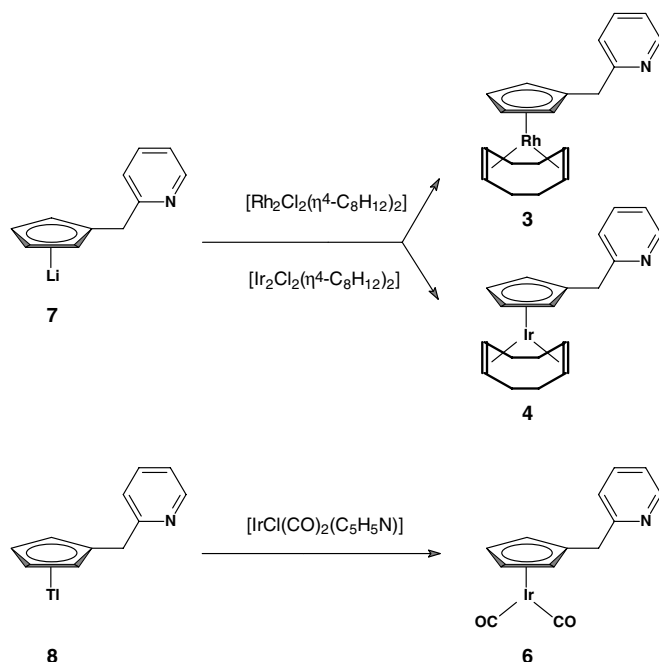M = Rh; L = η⁴-C₈H₁₂: **3**
M = Ir; L = η⁴-C₈H₁₂: **4**
M = Rh; L = CO: **5**
M = Ir; L = CO: **6**

2. Results and discussion

2.1. Preparation and characterization of the complexes 3, 4, and 6

Either 2-picolylcyclopentadienyllithium (**7**), derived by the reaction of 2-picolylcyclopentadiene with *n*-butyllithium, or 2-picolylcyclopentadienylthallium(I) (**8**), obtained by reacting 2-picolylcyclopentadiene with thallium(I) ethoxide, were tested in the reactions with the rhodium(I) and iridium(I) chlorides, $[RhCl(\eta^4\text{-}C_8H_{12})]_2$, $[IrCl(\eta^4\text{-}C_8H_{12})]_2$, and $[IrCl(C_5H_5N)(CO)_2]$, in order to prepare complexes **3**, **4**, and **6**. We found that **3** and **4**, are obtained in good yields, 63% and 58%, respectively, using the lithium derivative **7**. In the case of **6**, better yields (40%) are obtained using the thallium(I) derivative **8** (Scheme 1), as observed also by Rausch et al. [4] who have obtained the dicarbonyl rhodium(I) complex **5** by reacting the thallium derivative **8** with $[Rh_2Cl_2(CO)_4]$. All complexes are sufficiently thermally stable at the solid state to be manipulated at room temperature under dinitrogen without any apparent alteration.

Well resolved ^1H NMR were obtained which are consistent with the proposed structures (Table 1). In the case of **3** and **4** the chemical shifts of the vinyl protons (centred at δ 3.83 and 3.72 ppm, respectively), practically identical to those shown by the isostructural 9-anthrylmethylcyclopentadienyl derivatives **1** (M = Rh; $L_2 = \eta^4\text{-}C_8H_{12}$) ($\delta$ 3.84 ppm) and **1** (M = Ir; $L_2 = \eta^4\text{-}C_8H_{12}$) ($\delta$ 3.73 ppm) [1a], are observed at moderately higher fields than in the case of the Cp derivatives **9** [6] and **10** [7] (δ 3.97 and 3.78 ppm, respectively). This shows that the electron-donating power of the 2-picolyl-functionalized cyclopentadienyl ligand is moderately higher than that of Cp, but lower than that of Cp* ($[Rh(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_8H_{12})]$ [8]: δ 2.95 ppm, vinyl protons; $[Ir(\eta^5\text{-}C_5Me_5)(\eta^4\text{-}C_8H_{12})]$ [7]:

These facts parallel the CO stretching frequency variation that is observed passing from **5** (2042, 1976 cm^{-1}, nujol mull) and **6** (2042, 1976 cm^{-1}, nujol mull) to the corresponding Cp derivatives **11** (2051, 1987 cm^{-1}, neat) [9] and **12** (2037, 1957 cm^{-1}, neat) [10] and to the Cp* derivatives [Rh(η^5-C$_5$Me$_5$)(CO)$_2$] (2000, 1950 cm^{-1}) [11] and [Ir(η^5-C$_5$Me$_5$)(CO)$_2$] (2000, 1925 cm^{-1}) [6]. Expectedly, the substituent on the Cp ring has an impact on the bond order of the terminal carbonyl ligand as a consequence of influence it exerts on the electron density on the metal centre and then on the ability of the metal to back-donate electron density into the unfilled π^* molecular orbital of carbon monoxide.

The mass spectra of **3**, **4**, and **6** were obtained by ESI-MS (electro-spray ionization mass spectrometry). The spectrum of **3** shows an intense pseudomolecular peak, [M + H]$^+$, at m/z 368, while, both the spectra of **4** and **6** show a pattern of pseudomolecular peaks arising from the presence of the two iridium isotopes (^{191}Ir, 37.3%; ^{193}Ir, 62.7%): [M + H]$^+$ (^{193}Ir, m/z 458) and [M + H]$^+$ (^{191}Ir, m/z 456), in the case of **4**, and [M + H]$^+$ (^{193}Ir, m/z 406) and [M + H]$^+$ (^{191}Ir, m/z 404), in the case of **6**.

Scheme 1.

δ 2.73 ppm, vinyl protons). Expectedly, in all cases a moderate shift towards higher fields is observed on going from the rhodium(I) to iridium(I) derivatives.
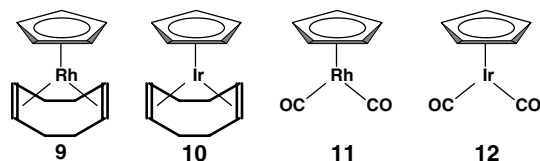

2.2. Electronic absorption spectra of complexes 3–6

The UV–Vis spectra (210–330 nm) of complexes **3–6** along with those of reference complexes **9–12** and of 2-picoline are reported in Fig. 1. The spectrum of 2-picoline is similar to that of benzene, although the band at 260 nm ($\pi^* \leftarrow \pi$ transition) is, in the case of 2-picoline, more intense and has a less resolved fine structure than that exhibited by benzene. The weak band expected for a $\pi^* \leftarrow n$ transition is observed only when the spectrum of 2-picoline is registered in the vapour phase [12]. Indeed, it shows two absorption regions whose relative intensities

Table 1
^{1}H NMR data for the complexes **3–6**[a]

Complex	δ (ppm), J/Hz
[Rh{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(η^4-C$_8$H$_{12}$)] (**3**)	8.47 (1H, s, H^1), 7.02 (1H, t, J_{HH} 8, H^3), 6.91 (1H, d, J_{HH} 7, H^4), 6.59 (1H, d, J_{HH} 8, H^2), 5.10 (2H, bs, H^7), 4.80 (2H, bs, H^6), 3.83 (4H, bs, vinylic protons of C$_8$H$_{12}$), 3.62 (2H, bs, H^5), 2.20 (4H, m, allylic protons of C$_8$H$_{12}$), 1.96 (4H, m, allylic protons of C$_8$H$_{12}$)
[Ir{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(η^4-C$_8$H$_{12}$)] (**4**)	8.45 (1H, s, H^1), 6.98 (1H, t, J_{HH} 8, H^3), 6.87 (1H, d, J_{HH} 7, H^4), 6.58 (1H, d, J_{HH} 8, H^2), 5.01 (2H, bs, H^7), 4.73 (2H, bs, H^6), 3.72 (4H, bs, vinylic protons of C$_8$H$_{12}$), 3.60 (2H, bs, H^5), 2.17 (4H, m, allylic protons of C$_8$H$_{12}$), 1.95 (4H, m, allylic protons of C$_8$H$_{12}$)
[Rh{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(CO)$_2$] (**5**)[b]	8.41 (1H, s, H^1), 7.01 (1H, t, J_{HH} 8, H^3), 6.73 (1H, d, J_{HH} 7, H^4), 6.58 (1H, d, J_{HH} 8, H^2), 5.17 (2H, bs, H^7), 4.79 (2H, bs, H^6), 3.49 (2H, bs, H^5)
[Ir{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(CO)$_2$] (**6**)	8.38 (1H, s, H^1), 6.98 (1H, t, J_{HH} 8, H^3), 6.75 (1H, d, J_{HH} 7, H^4), 6.58 (1H, d, J_{HH} 8, H^2), 5.07 (2H, bs, H^7), 4.68 (2H, bs, H^6), 3.48 (2H, bs, H^5)

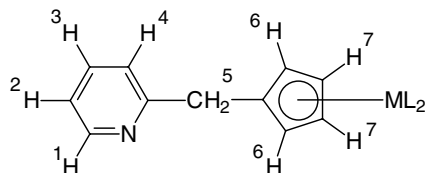[a] Spectra recorded in C$_6$D$_6$; s, singlet; m, multiplet; d, doublet.
[b] In the literature [4] the spectrum of **5** was registered in CDCl$_3$.

Fig. 1. Comparison of the UV–Vis spectrum of $[M\{\eta^5\text{-}C_5H_4(2\text{-}CH_2C_5H_4N)\}L_2]$ (—) 3–6 with the sum (—) of the spectra of 2-picoline (—) and of $[M(\eta^5\text{-}C_5H_5)L_2]$ (—) 9–12: (a) M = Rh, $L_2 = \eta^4\text{-}C_8H_{12}$; (b) M = Ir, $L_2 = \eta^4\text{-}C_8H_{12}$; (c) M = Rh, L = CO; (d) M = Ir, L = CO.

are very different. Region I (270–290 nm) is characterized by low intensity narrow pyridine-like bands and is due to a $\pi^* \leftarrow n$ transition of a nonbonding sp^2 electron of the nitrogen atom into the first unfilled π orbital of the pyridine ring. Region II, of higher intensity, occurs at about 240–270 nm, its diffuse broad bands resembling the spectra of some substituted benzenes. This absorption is due to a $\pi^* \leftarrow \pi$ transition resulting from $2p\pi$ electrons of the ring. On passing from vapour phase to solutions, especially in polar and hydrogen-bonding solvents, the $\pi^* \leftarrow n$ band of the spectra of 2-picoline is blue shifted and broadened, while the vibrational structure of the $\pi^* \leftarrow \pi$ transition is sharpened and red shifted. The shift of the $\pi^* \leftarrow n$ band, due to the formation of a hydrogen bond between the nitrogen nonbonding (sp^2) electrons and protic solvents, is sufficient to make the region I to shift towards the region II, thus resulting obscured by the latter. Moreover, on passing from *i*-octane to ethanol solution, the intensity of the first region bands decreases while that of the second region bands increases [13]. The UV–Vis absorption spec-

tra of the rhodium complexes 9 and 11 show two absorption bands which are most probably due to metal-cyclopentadienyl charge transfer transitions, while the absorption spectra of the iridium complexes 10 and 12 show only one band. The main features of the absorption spectra of complexes 3–6 are either the lack of the vibrational structure typical of the 2-picoline chromophore or the presence of an absorption tail which is more evident for the iridium derivatives 4 and 6. Moreover, the molar extinction coefficients of the absorption bands of the rhodium derivatives 3 and 5, which are associated with the cyclopentadienyl-metal sub-unit (220–230 nm and 280–290 nm, respectively), are lower than those observed in the case of the reference compounds 9 and 11. These observations become more evident if one compares the spectra of 3–6 with those resulting from the sum of the spectrum of 2-picoline and of the spectra of 9–12 (Fig. 1). The unresolved vibrational structure, the absorption tails, and the differences in the molar extinction coefficients are all indicative of the existence of some electronic interaction

between the 2-picolyl group and the cyclopentadienyl-metal sub-unit [14].

2.3. Electrochemical studies

Fig. 2 compares the voltammetric (CV) curves for 0.5 mM rhodium **3** (a) and **5** (b), and iridium **4** (c) and **6** (d) complexes in THF. All the curves, obtained under strictly aprotic conditions, display, in the region of positive potentials, a single one-electron anodic process. Such a process, on the basis of previous investigations of the
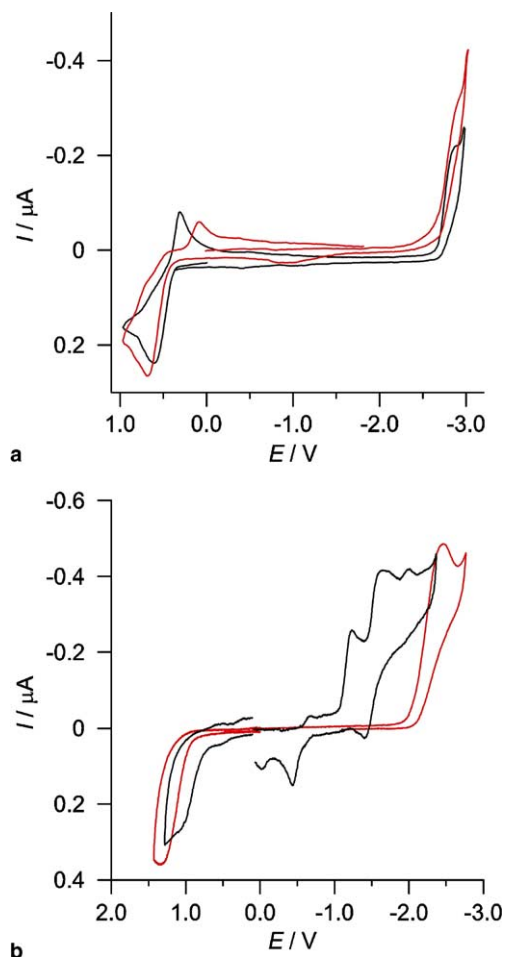
model compounds **9–12** and of analogous 9-anthrylmethyl-cyclopentadienyl rhodium and iridium derivatives [1c], is easily attributed to the oxidation of the metal centre and its reversibility is largely influenced by the nature of the ancillary ligands. The complexes containing 1,5-cyclooctadiene ligand showed in fact a reversible oxidation peak, located at relatively low potentials. Although chemically reversible, such processes display a rather large separation between the anodic peak and its cathodic counterpart. Typically, this happens when a slow heterogeneous electron transfer (ET) kinetics takes place, as observed when a significant structural rearrangement of the molecule is coupled to the ET process [15]. From the average value of the two peak potentials, the corresponding half-wave potentials were determined ($E_{1/2} = 0.45$ and 0.39 V, for **3** and **4**, respectively). In the case of the dicarbonyl complexes, **5** and **6**, the oxidation process is totally irreversible and, in line with the better electron accepting properties of CO ligands with respect to 1,5-cyclooctadiene, it is, in both cases, largely displaced to higher potentials with respect to the corresponding 1,5-cyclooctadiene complexes, **3** and **4**. The anodic peak potential (1.08 and 1.33 V, for **5** and **6**, respectively, measured at 1 V/s) was found to shift by ca 30 mV/decade towards more positive values as the scan rate was increased (between 0.5 and 200 V/s), suggesting that the irreversibility is due to chemical degradation of the electrogenerated radical cations. In the region of negative potentials, all species display, at similar potentials and close to the limit of base solution discharge (Table 2), a single irreversible cathodic peak, attributed to the reduction of the pyridyl moieties [16]. In the case of the dicarbonyl complexes (Fig. 2c and d), however, such a peak (not shown in the CV of Fig. 2c and d) is preceded by irreversible cathodic peaks associated with the reduction of the cyclopentadienyl-metal moiety. A similar irreversible behaviour has previously observed in the case of the model compounds **11** and **12**, and of the 9-anthrylmethylcyclopentadienyl rhodium and iridium analogues [1c].

2.4. Preparation of the ruthenium(II)–rhodium(I) hetero-bimetallic complex 13

As pointed out in the introduction, one of the purposes of the present research is to investigate the possibility to use the complexes **3–6** as nitrogen ligands to be coordinated to

Fig. 2. Cyclic voltammetric curves: (a) of 0.5 mM THF solutions of **3** (——) and **4** (——); (b) of 0.5 mM THF solutions of **5** (——) and **6** (——); scan rate, 1 V/s. Electrolyte, 0.05 M TBAH; working electrode, Pt disc ($r = 125$ μm); $T = 25$ °C.

Table 2
Redox potentials (E_p or $E_{1/2}$ (V) vs. SCE) of complexes 1–4, 0.5 mM, 0.05 M TBAH THF solutions

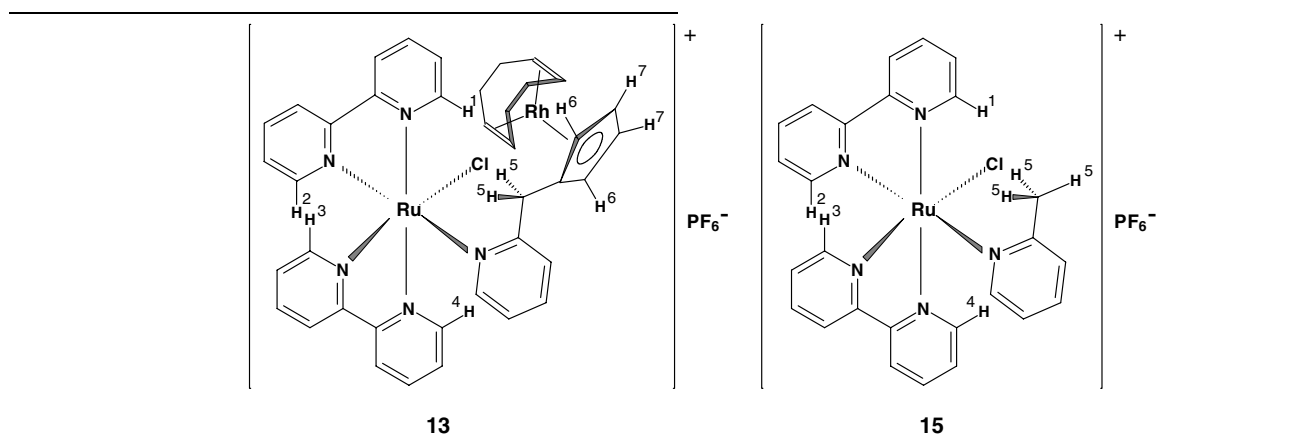| Complex	E (V)				
[Rh{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(η^4-C$_8$H$_{12}$)] (**3**)	0.60[a] (0.45)				−2.87[b]
[Ir{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(η^4-C$_8$H$_{12}$)] (**4**)	0.68[a] (0.39)				−2.91[b]
[Rh{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(CO)$_2$] (**5**)[b]	1.08[b]	−0.43	−1.23[b]	−1.59	−3.05[b]
[Ir{η^5-C$_5$H$_4$(2-CH$_2$C$_5$H$_4$N)}(CO)$_2$] (**6**)	1.33[b]		−2.47[b]		−3.01[b]

T, 25 °C; working electrode, platinum disc.
  [a] E_p, slow electron transfer process ($E_{1/2}$).
 [b] E_p, irreversible process.

another transition metal centres, thus succeeding in obtaining new covalently linked bimetallic systems. In this connection, assemblies resulting from the coordination of the compounds **3–6**, which are either electron-donors or electron-acceptors (see Section 2.3), to a ruthenium(II) centre, whose pyridine and 2,2′-bipyridine derivatives have excellent photo-physical properties and are either good electron-acceptors or good energy-donors [17], appeared interesting. Various attempts to do this trying to replace one or two chlorides by the picolyl rhodium or iridium complexes **3–6**, starting from ruthenium(II) complexes like [Ru(bipy)₂Cl₂] in the presence of chloride abstracting

bridging ligands), we succeeded in obtaining the red-brown bimetallic complex **13** by reacting the nitrosyl complex [RuCl(bipy)₂(NO)][PF₆]₂ **14** [19] first with potassium azide and then with the rhodium(I) complex **3** (Scheme 2). The model compound **15**, which carries a 2-picoline molecule instead of **3**, was prepared by the same synthetic method (Scheme 2). Complexes **13** and **15** are quite sensitive to air and moisture but not to temperature and then can be stored at room temperature, under argon atmosphere. Both complexes were characterized by elemental analysis, ¹H NMR (acetone-d_6), and ESI-MS (electro-spray ionization mass spectrometry).

13　　　　　　　　　　　　　　　　　　　　　**15**

reagents, failed. Instead, adopting the method described by Meyer et al. [18] for the preparation of a series of complexes of general formula [(bipy)₂ClRu(L)RuCl-(bipy)₂][PF₆]₂ 2H₂O (bipy = 2,2′-bipyridine; L = dinitrogen

The ¹H NMR spectrum of **13** shows that the four non-equivalent protons H¹–H⁴ give rise to two splitted signals centred at δ 10.26 and 9.82 ppm, respectively. Analogously, in the case of **15**, these protons give rise to two signals
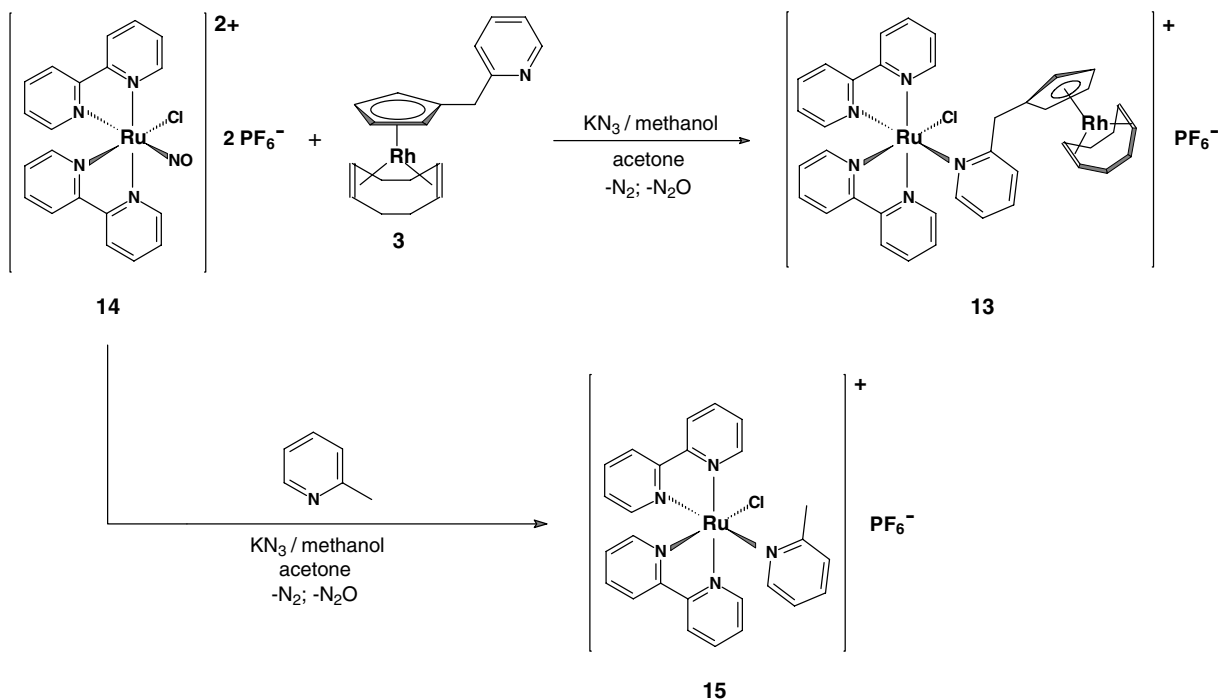
Scheme 2.

centred at δ 10.20 and 9.80 ppm. The shift of the resonances of these protons to lower fields as a consequence of the coordination to ruthenium is evident on comparison with the chemical shift of the same protons in free 2,2′-bipyiridine (δ 8.59 ppm) [20]. The resonances of all the other aromatic protons appear as a multiplet ranging from δ 8.87 to 7.22 ppm in the case of **13**, and from δ 8.85 to 7.26 ppm, in the case of **15**. The spectrum of **15** shows, finally, only one more singlet (δ 2.87 ppm) due to 2-picoline methyl protons, H[5]. The spectrum of **13**, instead, is more complex owing to the resonances due the protons of the (η^5-2-picolylcyclopentadienyl)(η^4-cycloocta-1,5-diene)rhodium(I) 'ligand'. The signals associated with H[5], H[6], and H[7] appear as three singlets at δ 3.67, 5.03, and 5.24 ppm, respectively, each of them integrating for two protons. The resonances of these protons are slightly shifted to low field if compared with those observed for free **3**. The olefinic protons of 1,5-cyclooctene give rise to a broad one-line signal (δ 3.83 ppm), whose integral accounts for four protons, while the allylic ones give rise to a multiplet centred at δ 2.09 ppm. These chemical shifts are practically identical to those of free **3**.

Good mass spectra of complexes **13** and **15** were obtained by ESI-MS technique. In both cases the pseudo-molecular $[M + H]^+$ peaks are present, showing the expected multiplicity due to the natural abundance of ruthenium seven isotopes (^{96}Ru, ^{98}Ru, ^{99}Ru, ^{100}Ru, ^{101}Ru, ^{102}Ru, ^{104}Ru) (see Section 4). In addition, both the mass spectra of **13** and **15** show also some peaks at m/z higher than the expected ones, which is indicative of the presence of some unknown impurities which could not be completely eliminated even after repeated dissolution/precipitation of the products. Accordingly, not so good elemental analyses are obtained.

3. Concluding remarks

The ^{1}H NMR and IR features of the 2-picolylcyclopentadienyl derivatives of rhodium(I) and iridium(I) **3–6**, which can be prepared in satisfactory yields, indicate that the 2-picolylcyclopentadienyl ligand is a better electron-donor than Cp but lower than that of other known RCH$_2$Cp ligands. Furthermore, the UV–Vis absorption spectra of **3–6** show that the presence of the methylene group as a spacer between the 2-pyridyl group and the cyclopentadienyl-metal moiety does not prevent the electronic communication between the two sub-units, as already observed in the case of various 9-anthrylmethylcyclopentadienyl derivatives of rhodium(I) and iridium(I) of general formula **1**, in which again the 9-anthryl group and the cyclopentadienyl-metal moiety are separated by a methylene fragment [1a]. If one takes into account the extension of the tail and the entity of the loss of the vibrational structure of the 2-picolylinic chromophore, it is evident that the strength of the electronic interaction between the 2-picolyl fragment and the cyclopentadienyl-metal sub-unit depends upon the nature of the metal centre, being higher in the case of the iridium(I) complexes **4** and **6**, than in the case of the rhodium(I) derivatives **3** and **5**, and increases passing from the 1,5-cyclooctadiene derivatives, **3** and **4**, to the dicarbonyl complexes **5** and **6**.

The study of the CV electrochemical behaviour of **3–6** shows that all these complexes undergo either metal-centred oxidations or 2-picolyl-centred reductions, the last occurring anyway at markedly negative potentials. Interestingly, the complexes **5** and **6**, i.e., the dicarbonyl derivatives, also undergo metal-centred reductions at quite accessible potentials, thus resulting either good electron-donors or good electron-acceptors (Scheme 3). On this base, the compounds **3–6** appear interesting candidates to be employed as building blocks for assembling new two-component molecular entities in which they could behave as a control unit capable of modifying the physical properties of the other sub-unit (light emitting properties, charge transfer, redox properties, etc.). In this connection, the synthesis of the ruthenium(II)–rhodium(I) bimetallic complex **13** shows that the complexes **3–6** can indeed be
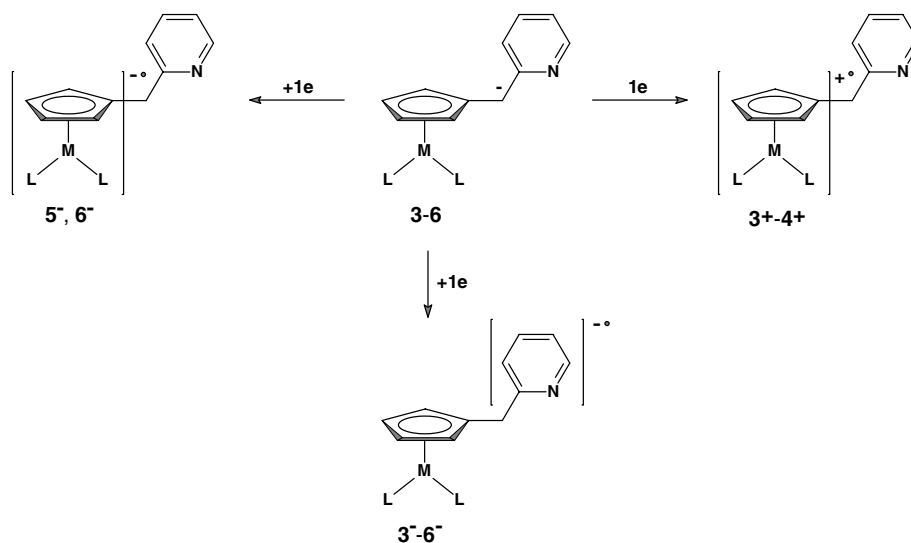
Scheme 3.

used as ligands to be coordinated to other transition metal centres through the picolinic nitrogen atom thus giving rise to bi-functional large molecules, and, most importantly, the work points out the potential utility of the 2-picolylcyclopentadienyl ligand for the development of a convenient means of assembling a variety of bimetallic complexes.

4. Experimental details

4.1. General procedures

The reactions and manipulations of organometallics were carried out under dinitrogen or argon using standard techniques. All solvents were dried and distilled prior to use following standard procedures. Microanalyses were performed by the Laboratorio di Microanalisi of the Dipartimento di Chimica Bioorganica e Biofarmacia (University of Pisa). ^{1}H NMR spectra were run at 200 MHz on a Varian Gemini 200 instrument. Infrared spectra were obtained by a FT-IR Perkin–Elmer 1750 spectrometer. The ESI-MS (electro-spray ionization mass spectrometry) spectra were obtained by a Perkin–Elmer Sciex API III *plus* triple quadrupole mass spectrometer (Sciex Co., Thornhill, Ont., Canada) equipped with an API ion source and an ionspray interface. The spectra were obtained under the following experimental conditions: ionspray voltage, 5.5 kV; orifice voltage, 35 or 60 V. The UV–Vis absorption spectra (210–330 nm) were measured at room temperature on dinitrogen-saturated ethanol solutions (5×10^{-5}–1×10^{-4} M) using a Perkin–Elmer UV/VIS LAMDA EZ 201 spectrophotometer with a resolution of 2 nm.

2-Picolylcyclopentadiene [4], 2-picolylcyclopentadienyl-thallium(I) (**8**) [4] [*owing to their toxicity, all thallium derivatives must be handled with care*], (η^5-2-picolylcyclopentadienyl)dicarbonylrhodium(I) (**5**) [4], di-μ-chlorobis-(η^4-cycloocta-1,5-diene)dirhodium(I) [21], di-μ-chlorobis(η^4-cycloocta-1,5-diene)diiridium(I) [22], chlorodicarbonyl(pyridine)iridium(I) [10], (η^5-cyclopentadienyl)(η^4-cycloocta-1,5-diene)rhodium(I) (**9**) [6], (η^5-cyclopentadienyl)(η^4-cycloocta-1,5-diene)iridium(I) (**10**) [7], (η^5-cyclopentadienyl)dicarbonylrhodium(I) (**11**) [9], and (η^5-cyclopentadienyl)dicarbonyliridium(I) (**12**) [10], potassium azide [23], bis(2,2'-bipyridine)chloronitrosylruthenium(II)-bis-(hexafluorophosphate) (**14**) [18] were prepared as reported. *n*-Butyllithium 1.6 M in hexane (Aldrich) was used as received. 2-Picoline (Aldrich) was distilled immediately prior to use. All column chromatographies were carried out on alumina (Aluminum oxide 90, 70–230 mesh, MERCK). For the electrochemical experiments, the solvent was distilled into the electrochemical cell, just prior to use, using a trap-to-trap procedure. Tetrahydrofuran (THF, LiChrosolv, Merck) was treated according to a procedure described elsewhere [24]. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (FLUKA, puriss.), the supporting electrolyte, was used as received.

4.2. Electrochemical instrumentation and measurements

The one-compartment electrochemical cell was of air-tight design with high-vacuum glass stopcocks fitted with either Teflon or Viton O-rings in order to prevent contamination by grease. The connections to the high-vacuum line and to the Schlenk containing the solvent were obtained by spherical joints also fitted with O-rings. The pressure in the electrochemical cell, prior to performing the trap-to-trap distillation of the solvent, ranged typically from 1.0 to 2.0×10^{-5} mbar. The working electrode consisted either of a 0.6 mm-diameter platinum wire (0.15 cm^2 approximately) sealed in glass or a platinum disc microelectrode ($r = 125$ μm) also sealed in glass. The counter electrode consisted of a platinum spiral and the quasi-reference electrode was a silver spiral. The quasi-reference electrode drift was negligible for the time required by a single experiment. Both the counter and the reference electrode were separated from the working electrode by ∼0.5 cm. Potentials were measured with the ferrocene standard and are always referred to saturated calomel electrode (SCE). $E_{1/2}$ values correspond to ($E_{pc} + E_{pa}$)/2 from CV. For irreversible peaks, the peak potential, E_p, is given, measured at 0.5 V s^{-1}. Ferrocene was also used as an internal standard for checking the electrochemical reversibility of a redox couple. Voltammograms were recorded with an AMEL Model 552 potentiostat or a custom made fast potentiostat controlled by either an AMEL Model 568 function generator or an ELCHEMA Model FG-206F. Data acquisition was performed by a Nicolet Model 3091 digital oscilloscope interfaced to a PC. Temperature control was accomplished within 0.1 °C with a Lauda RLS thermostat.

4.3. Synthesis of (η^5-2-picolylcyclopentadienyl)-(η^4-cycloocta-1,5-diene)rhodium(I) (3)

A solution of *n*-butyllithium (1.6 ml, 1 mmol) in 10 ml of diethyl ether is added drop wise to a solution of 2-picolyl-cyclopentadiene (0.16 g, 1.0 mmol) in 15 ml of diethyl ether, at −35 °C. The mixture is stirred at this temperature for 30 min and than for 2 h at room temperature. A suspension of di-μ-chlorobis(η^4-cycloocta-1,5-diene)dirhodium(I) (0.29 g, 0.59 mmol) in 10 ml of diethyl ether is added to the mixture, at −35 °C. Afterwards, the reaction mixture is stirred at the same temperature for 30 min, than for 12 h at room temperature, and finally dried under reduced pressure. The residue is extracted with 20 ml of benzene and filtered. The benzenic extract is dried under reduced pressure to leave a residue that is dissolved in 2 ml of benzene and purified by column (internal diameter, 10 mm; length, 300 mm) chromatography on alumina using benzene as eluant, under dinitrogen atmosphere. The first band which elutes gives **3** (0.27 g, 0.74 mmol; 63% yield) as a microcrystalline solid. Anal. Calc. for C$_{19}$H$_{22}$NRh: C, 62.13; H, 6.04; N 3.81. Found: C, 62.10; H, 6.00; N 3.75%; IS-MS, *m/z*: 368 [M + H]$^+$.

4.4. Synthesis of (η^5-2-picolylcyclopentadienyl)-(η^4-cycloocta-1,5-diene)iridium(I) (**4**)

This preparation is carried out exactly as reported for the preparation of **3**, but using di-μ-chlorobis(η^4-cyclo-octa-1,5-diene)iridium(I) (0.4 g, 0.59 mmol). The only difference is that in this case the crude reaction residue is dissolved in 2 ml of a 9/1 (v/v) benzene/chloroform mixture and purified by column (internal diameter, 10 mm; length, 300 mm) chromatography on alumina using a 9/1 (v/v) benzene/chloroform mixture as eluant, under dinitrogen atmosphere. The first band which elutes gives **4** (0.32 g, 0.70 mmol; 58% yield) as a microcrystalline solid. Anal. Calc. for $C_{19}H_{22}NIr$: C, 49.98; H, 4.86; N, 3.07. Found: C, 49.91; H, 4.80; N, 3.00%. IS-MS, *m/z*: 456 $[M + H]^+$ (^{191}Ir), 458 $[M + H]^+$ (^{193}Ir).

4.5. Synthesis of (η^5-2-picolylcyclopentadienyl)-dicarbonyliridium(I) (**6**)

A mixture of 2-picolylcyclopentadienyltallium(I) (**8**) (0.35 g, 1.00 mmol), chlorodicarbonyl(pyridine)iridium(I) (0.36 g, 1.00 mmol), and benzene (25 ml) is stirred for 12 h, at room temperature; then filtered and dried under reduced pressure. The residue is dissolved in 3 ml of a 8.5/1.5 (v/v) *n*-hexane/ethyl acetate mixture and purified by column (internal diameter, 10 mm; length, 300 mm) chromatography on alumina using a 8.5/1.5 (v/v) *n*-hex-ane/ethyl acetate mixture as eluant, under dinitrogen atmosphere. From the first band eluted, **6** (0.16 g, 0.40 mmol; 40% yield) is obtained as a viscous golden yellow oil. Anal. Calc. for $C_{13}H_{10}NO_2Ir$: C, 38.61; H, 2.49; N, 3.46. Found: C, 38.55; H, 2.40; N, 3.40%. IS-MS, *m/z*: 404 $[M + H]^+$ (^{191}Ir), 406 $[M + H]^+$ (^{193}Ir). IR (Nujol): 2913 (w); 2033 (s); 1966 (s); 1461 (s); 1377 (s); 722 (s) cm^{-1}.

4.6. Synthesis of bis(2,2'-bipyridine)[(η^5-2-picolylcyclo-pentadienyl)(η^4-cycloocta-1,5-diene)rhodium(I)]-chlororuthenium(II)-(hexafluorophosphate) (**13**)

A solution of 2.2 mg (0.03 mmol) of potassium azide in 1 ml of methanol is drop wise added, at room temperature, to the yellow solution of 21 mg (0.03 mmol) of bis(2,2'-bipyridine)chloronitrosylruthenium(II)bis(hexafluorophos-phate) (**14**) in 5 ml of argon-saturated acetone. The dark red reaction mixture is stirred for 30 min, at room temperature. The mixture is then added to the solution of 110 mg of **3** (0.3 mmol) in 5 ml of acetone. The resulting mixture is stirred at 50 °C for 30 min. After cooling to room temperature, the reaction mixture is added to 100 ml of anhydrous diethyl ether. This makes **13** to precipitate as a dark red microcrystalline solid, which is separated and dried under vacuum. Yield, 2.9 mg; 10%. Anal. Calc. for $C_{39}H_{38}N_5ClF_6PRuRh$: C, 48.74; H, 3.98; N, 7.29. Found: C, 49.50; H, 4.20; N, 7.55%. IS-MS, *m/z*: 810 (5.5%) $[M + H]^+$ (^{96}Ru), 812 (1.9%) $[M + H]^+$ (^{98}Ru), 813 (12.7%) $[M + H]^+$ (^{99}Ru), 814 (12.6%) $[M + H]^+$ (^{100}Ru), 815 (17.0%) $[M + H]^+$ (^{101}Ru), 816 (31.6%) $[M + H]^+$ (^{102}Ru), 818 (18.7%) $[M + H]^+$ (^{104}Ru).

4.7. Synthesis of bis(2,2'-bipyridine)(2-picoline)-chlororuthenium(II)-(hexafluorophosphate) (**15**)

The title compound is prepared exactly as reported for the preparation of **13**. Starting from 2.2 mg (0.03 mmol) of potassium azide in 1 ml of methanol, 21 mg (0.03 mmol) of bis(2,2'-bipyridine)chloronitrosylruthenium(II)bis(hexa-fluorophosphate) in 5 ml of acetone, and a solution of 28 mg of 2-picoline (0.3 mmol) in acetone (5 ml), 3.1 mg of **15** (15% yield) are obtained as a dark red microcrystal-line solid. Anal. Calc. for $C_{26}H_{23}N_5ClF_6PRu$: C, 45.46; H, 3.37; N, 10.19. Found: C, 46.50; H, 3.90; N, 10.45%. IS-MS, *m/z*: 536 (5.5%) $[M + H]^+$ (^{96}Ru), 538 (1.9%) $[M + H]^+$ (^{98}Ru), 539 (12.7%) $[M + H]^+$ (^{99}Ru), 540 (12.6%) $[M + H]^+$ (^{100}Ru), 541 (17.0%) $[M + H]^+$ (^{101}Ru), 542 (31.6%) $[M + H]^+$ (^{102}Ru), 544 (18.7%) $[M + H]^+$ (^{104}Ru).

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