Novel hetero-polymetallic derivatives of palladium bearing pyridylthioether fragments incorporating a $Fe_2(CO)_6$ cluster core as ligand

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Abstract

The complexation of poly(pyridylthioether) incorporating a $Fe_2(CO)_6$ cluster core with palladium derivatives in different oxidation states afforded novel hetero-polymetallic complexes.
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The synthesis of chelating ligands carrying potentially coordinating nucleophiles and encapsulating metal clusters might represent an important step in the preparation of polymetallic substrates. Moreover, the preparation of composites in which the organic part is constituted by dendrimers of increasing complexity which however maintain their intrinsic coordinating capability leads to derivatives representing a new class of polymetallic complexes with interesting applications in the field of catalysis [1], molecular recognition [2] and photoactive device engineering [3].

We have recently published the synthesis and characterization of poly(pyridylthioether) dendrimers incorporating a $Fe_2(CO)_6$ core [4]. This important result makes the preparation of hetero-polymetallic derivatives accessible and this paper deals with the synthesis, isolation and characterization of new complexes bearing a $Fe_2(CO)_6$ in the core and palladium atoms in various oxidation states at the peripheral termini. The coordinative capability of the pyridylthioether derivatives with respect to palladium atom in different oxidation states is well recognized and a great deal of papers supporting this observation are available in the

literature [5]. As a preliminary study aiming at the preparation of precursor complexes, we have synthesized and characterized the substrates reported in Scheme 1. Moreover, we have carried out a detailed analysis of their fluxional behavior in solution by means of NMR technique.

As can be seen in Scheme 1 the connection between pyridylthioether fragments and the $Fe_2(CO)_6$ core is assured by phenyl groups which may allow an electron transfer between the molecular termini. In this respect, the coordination of palladium atoms in different oxidation states would represent an interesting approach to possible future electrochemical applications.

The synthesis of **L** derivative is reported elsewhere [4], while the complexes **1–5** were prepared according to a well-tried synthetic protocol. Thus, the olefin palladium(0) derivatives **1–3** were obtained in dried acetone under inert atmosphere (Ar) by mixing a stoichiometric amount of $Pd_2(DBA)_3$, **L** and a slight excess of the appropriate olefin (ol = tetramethylethylenetetracarboxylate tmetc, maleic anhydride ma, naphthoquinone nq). The resulting solution was stirred for a couple of hours, evaporated under reduced pressure, treated with activated carbon, filtered on celite filter and eventually the complexes were precipitated by addition of diethyl ether [6].

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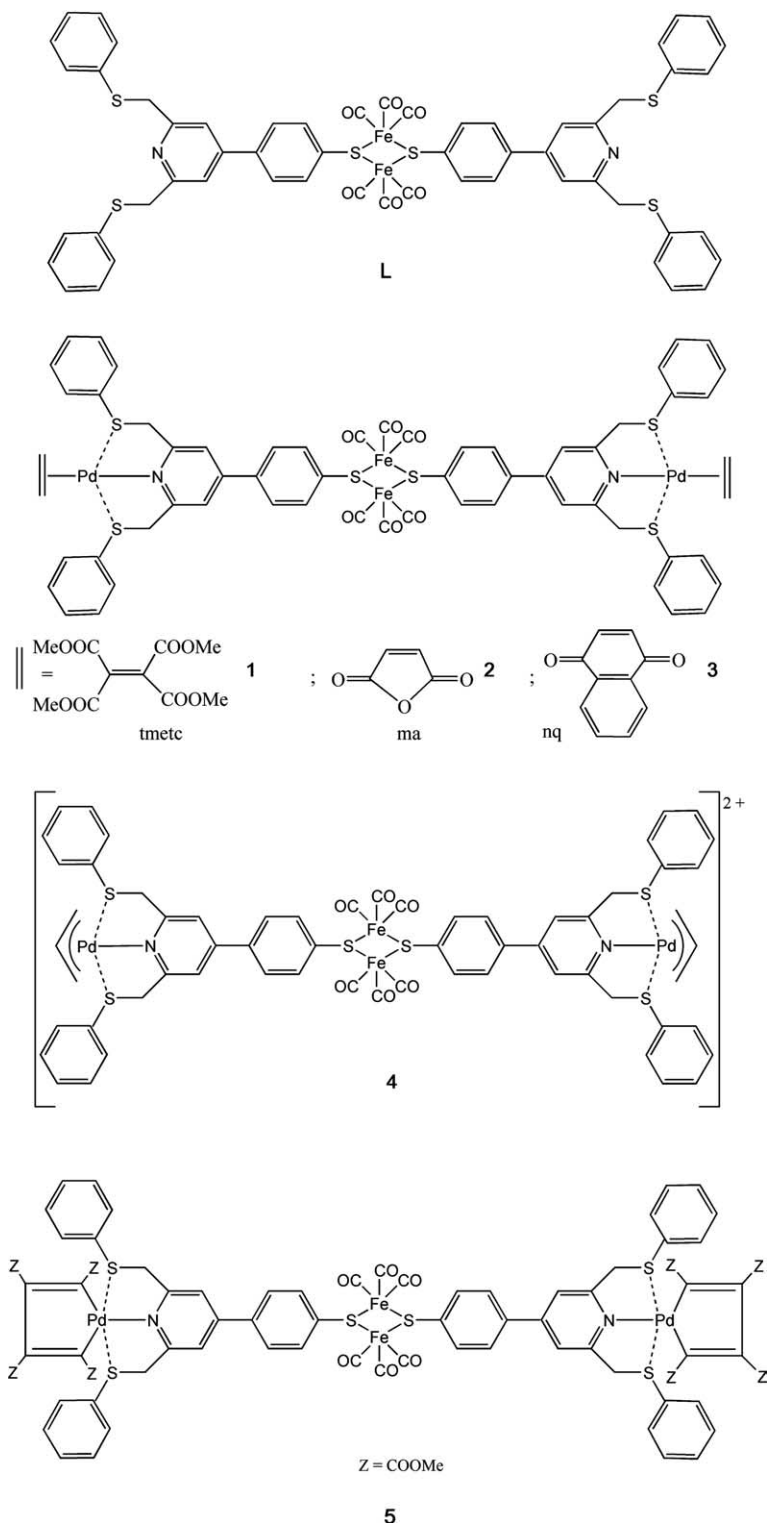
Scheme 1.

It is noteworthy that the Pd(0) dendritic complexes may easily reach a remarkable degree of complexity since no solubility problems induced by the increasing charge of the substrates arise in these cases [6b–6d].

One of the alternative paths to palladium(0) derivatives is represented by the reaction of amination of allyl complexes carried out in the presence of an activated olefin

[7] and in this respect we have studied the reactivity of Pd(0) allyl complexes bearing dendritic wedges of increasing size carrying in the core the S–N–S coordinating system as ancillary ligands [8]. We have therefore synthesized complex **4** under inert atmosphere (Ar) in anhydrous CH_2Cl_2 by adding to a solution of **L** and silver triflate (**L**: Ag OTf, 1:2) a stoichiometric amount of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$.

Table 1
Selected IR and NMR data for the complexes **1–5**

Complex	Yield	^{1}H NMR	^{13}C NMR	IR
1	78% yellow-orange	3.61 (s, 24H, COOCH_3) 4.65 (s, 8H, CH_2–S)	53.2 (CH_3) 44.3 (CH_2–S) 208.3 (Fe–CO)	2075 (s), 2038 (vs), 1992 (s), 1721 (vs), 1599 (m) cm^{-1}
2	77% yellow-orange	4.27 (s, 4H, CH) 4.46 (s, 8H, CH_2–S)	45.3 (CH) 44.1 (CH_2–S) 208.4 (Fe–CO)	2072 (s), 2033 (vs), 1991(s), 1798 (s), 1599 (m) cm^{-1}
3	41% yellow-orange	4.92 (bs, 4H, CH) 4.39 (s, 8H, CH_2–S)	62.3 (CH) 45.8 (CH_2–S) 208.7 (Fe–CO)	2079 (s), 2038 (vs), 1992 (s), 1648 (s), 1591 (m) cm^{-1}
4	68% yellow-orange	4.36 (d, 8H, $J = 8.7$ Hz, H-*syn* + H-*anti*) 4.82 (s, 8H, CH_2–S) 6.08 (quintet, 2H, $J = 9.6$ Hz, H^2-All)	68.8 (CH_2-All) 119.2 (CH-All) 46.5 (CH_2–S) 208.7 (Fe–CO)	2073 (s), 2035 (vs), 1996 (s), 1598 (m) cm^{-1}
5	89% yellow-orange	3.38 (bs, 12H, COOCH_3 α) 3.68 (s, 12H, COOCH_3 β) 4.57 (bs, 8H, CH_2–S)	47.2 (CH_2–S) 53.3 53.1 (CH_3) 208.5 (Fe–CO)	2072 (s), 2037 (vs), 1998 (s), 1727 (s), 1593 (m) cm^{-1}

The reaction mixture was stirred for 2 h in the dark, filtered and dried under reduced pressure. The residue was dissolved in a small volume of CH$_2$Cl$_2$, treated with activated carbon and filtered on celite filter. Addition of diethyl ether to the solution causes the precipitation of the yellow-orange product **4**.

The formation of metallacyclic complexes of palladium(II) represents a key intermediate in the annulation reaction [9] and in the synthesis of conjugated dienes [10]. In this respect, the synthesis of complex **5** is aimed at the possible use of this sort of derivatives in palladium catalyzed reactions involving unsaturated molecules. An equimolecular amount of [PdC$_4$(COOMe)$_4$]$_n$ [11] was added under inert atmosphere (Ar) to a solution of **L** in anhydrous CH$_2$Cl$_2$. The resulting mixture, stirred for a couple of hours, leads to the formation of complex **5** which was isolated by addition of diethyl ether to the concentrated reaction solution.

The yields and the spectral characteristics of the complexes are reported in Table 1.

As stated elsewhere [4] the complexity of the synthesized structures hampers their analytical characterization, no mass spectrometric studies (MALDI-TOF, Electrospray ionization) are indeed successful in the cases of the synthesized complexes. Moreover, at variance with the dendrimers incorporating the Fe-carbonyl cluster as the sole metal carrying moiety [4], the elemental analysis data of the heavier palladium derivatives under study are uncertain and not clear-cut. Furthermore, the temperature dependent ^{1}H NMR studies in CD$_2$Cl$_2$ give indication about the structure of the complexes and the rearrangements they undergo in solution. In this respect, it is convenient first to describe the fluxional behavior of **L** which exists in solution in four different structures of different energy as represented in Fig. 1.

The *syn* isomers represent the two indistinguishable intermediates in the wing alternating movement leading to the two *anti*-derivatives which can be considered the most stable species, as shown by other authors in the case of similar derivatives to those reported in this paper [12,13]. In other words, the *syn* structures themselves are probably characterized by different energy but owing to their symmetry it is not possible to assign the related absolute configuration. However, the molecular model seems to indicate that a remarkable steric interference arises between *R* groups in the case of the *syn* (a,a) isomer, suggesting that the *syn* (e,e) derivative should be the most probable intermediate in the interconversion between the two *anti*-isomers.

As for the Pd(0) olefin derivatives, we will discuss in detail the fluxional behavior of complex **1** owing to the bulkiness, the symmetry and the peculiar intensity of the proton signals of the COOCH_3 protons of tmetc. The other olefin complexes (**2**, **3**) behave analogously but their ^{1}H NMR spectra are less significant due to the poor quality of the signals of the two olefin protons with respect to the overwhelming aromatic signals. The R.T. ^{1}H NMR spectrum of complex **1** displays two singlets at 3.61 ppm (COOCH_3 olefin protons) and at 4.65 ppm (CH_2S protons). The low temperature spectrum (193 K) displays a broadened signal ascribable to CH_2S protons and three singlets at 3.42, 3.58 and 3.66 ppm (1:1:2 relative intensity) which are related to the methyl groups of the four olefin carboxylates. The most obvious interpretation would suggest a "frozen" open structure in which the uncoordinated part of the potentially terdentate S–N–S ligand induces an asymmetry between the left and the right part of the complex. Moreover, the sulfur atom at 293 K slows down its absolute configuration inversion rate and this further asymmetry renders the olefin COOCH_3 protons of the same part of the substituent at sulfur magnetically non-equivalent to those lying on the opposite side of the substituent with respect to the complex main plane. The signal at 3.66 ppm (absolute intensity = 6) refers to two isochronous unidentified methyl groups. No isomers due to **L** conformation are in this case detected at any safely attainable temperature.[1]

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[1] In related systems two well characterized signals ascribable to CH_2S protons are detectable (an AB system and a broadened singlet). Such a situation was traced back to the formation at low temperature of a derivative in which only one wing of the S–N–S ligand is coordinated [14].
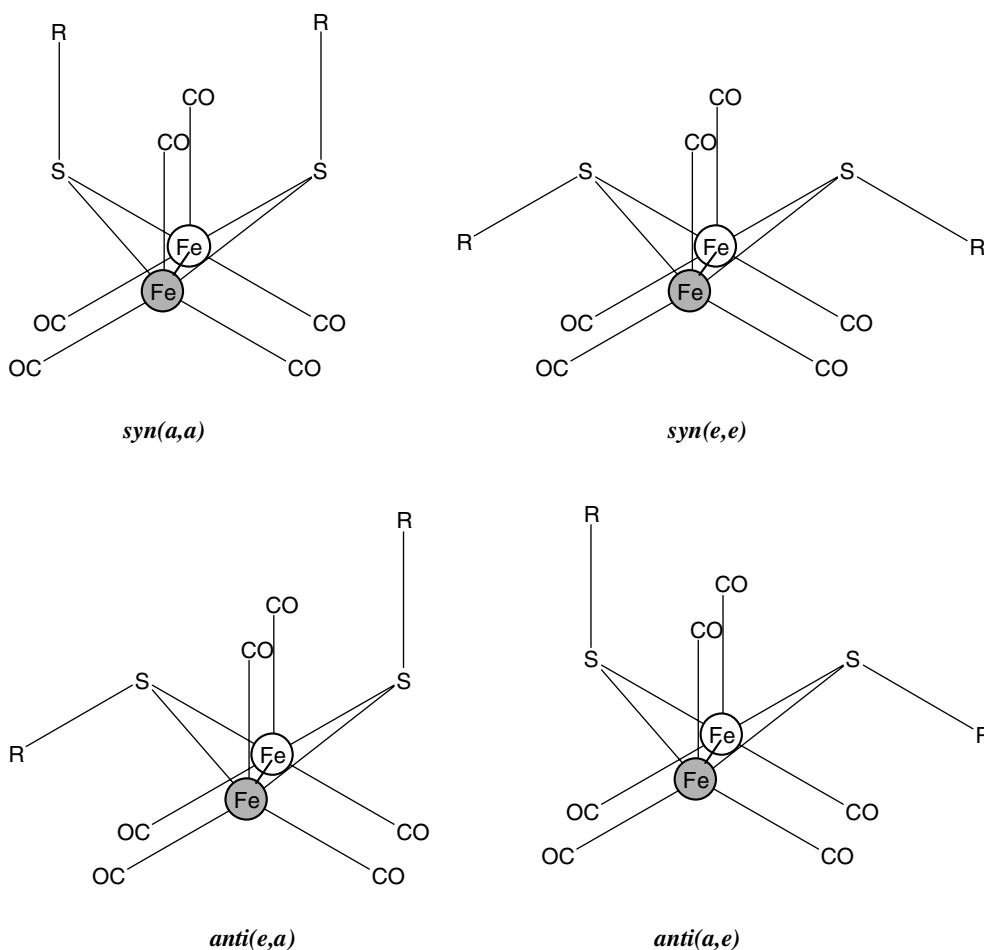
Fig. 1. Topological representation of the possible isomers of ligand **L** that are present in solution.

Complex **4** undergoes the typical fluxional rearrangement of potentially terdentate pyridylthioether allyl derivatives which was described in detail elsewhere [6a]. The allyl fragment gives rise to a peculiar couple of signals which are traced back to the allyl *syn* and *anti* and to the central H^2 protons. In particular no noticeable change is observed on decreasing the temperature since only a slight broadening of the doublet centered at 4.36 ppm (*syn* + *anti* allyl protons) is observable. The H^2 allyl proton resonates as a quintet at 6.1 ppm while the CH_2S protons give rise to a sharp singlet at 4.82 ppm. This feature is clearly interpreted as an η^3–η^1–η^3 isomerism of the allyl fragment induced by the fast wind-screen wiper like movement of the S–N–S ligand wings in the alternate attack of the sulfur to the tetracoordinate palladium atom. Under these circumstances, the ease of attack of the incoming uncoordinated sulfur does not allow any "freezing" of the open unsymmetrical complex and no differences between the chemical shifts nor formation of an AB signal induced by the diastereotopic (when coordinated) CH_2S protons are detected [6a,15]. It is however noteworthy that the crystal structure determination of the palladium(II) allyl derivative carrying the terdentate pyridylthioether ligand indicates that the complex precipitates as a bidentate [15], the η^1-allyl species with

the three-coordinated ligand being a low energy intermediate in the fluxional process. It is moreover apparent that also in this case the isomer distribution of the ligand **L** does not affect the isomer distribution of the complex since no indication of other species in solution is observed even at the lowest safely obtainable temperature (178 K).

The aliphatic region of the 298 K ^{1}H NMR spectrum of complex **5** in CD_2Cl_2 displays three well defined singlets at 3.36, 3.61 and 4.75 ppm of relative intensity 2:2:1, respectively. The high field signals are attributable to the α (3.36 ppm) and β (3.61 ppm) $COOCH_3$ protons of the metallacyclopentadienyl moiety while the thioether protons CH_2–S resonate at 4.75 ppm. On decreasing the temperature the singlet at 336 splits into two singlets, while the singlet at 4.75 broadens. At 193 K the spectrum displays four signals at 3.22, 3.24, 3.40 and 3.43 ppm ($COOCH_3$ α protons), a singlet at 3.64 ppm ($COOCH_3$ β protons) and a couple of doublets centered at 4.46 ppm ($J = 14.9$ Hz), ascribable to CH_2–S protons. Since no signals attributable to non-coordinated CH_2–S protons are detected and the $COOCH_3$ in α are observed as a doublet of doublets, we conclude that we are in the presence of a peculiar rearrangement which renders the two wings of the S–N–S moiety equivalent and "coordinated" but induces asymmetry

in the palladacyclopalladate α COOCH_3 protons. In our opinion, a plausible explanation should be found in the intimate fluxional mechanism which takes into account the formation of a T-shaped N-centered intermediate followed by a roundabout movement which makes the two wings of the ligand equivalent, whereas the carbons α to palladium are still different since their position with respect to the original *trans* atom does not change. Some sort of residual interaction between the sulfur atoms and palladium remains however operative, and the presence of a couple of doublets at 4.46 ppm witnesses this behavior. This phenomenon was already observed [8] and its interpretation allows only in this case a detailed description of the intimate mechanism of the fluxional rearrangement in palladium complexes bearing potentially terdentate pyridylthioether ligands. Moreover,in our opinion the splitting of the signal of α COOCH_3 protons into two further doublets of similar intensity might be traced back to the "freezing" at low temperature of the less energetic species derived from the ligand *anti*-conformation which was demonstrated to be the most stable among all the others available.

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