ELSEVIER

Journal of Organometallic Chemistry 632 (2001) 3–10

Journal of Organo metallic Chemistry

www.elsevier.com/locate/jorganchem

Thiophene versus aryl coordination in tricarbonylmanganese complexes with interesting non-linear optical properties

Luis F. Veiros

Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisbon, Portugal

Received 30 January 2001; accepted 16 March 2001

Dedicated to Professor Alberto Romão Dias on the occasion of his 60th birthday

---

Abstract

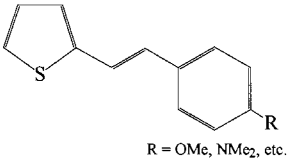
Molecular orbital calculations performed with the B3LYP HF/DFT hybrid functional are used to study the bonding and coordination geometry of a π ligand containing a large delocalised system (X = 1-(thiophenyl),2-(aryl)ethene) to tricarbonylmanganese(I) in complexes $[(\eta^n\text{-X})Mn(CO)_3]^+$. The coordination mode of X depends on the nature of the substituent on the *para* aryl carbon with respect to the ethene position. A hydroxyl group (R = OH) favours the η^5 coordination through the thiophene ring, while an amino substituent ($R = NH_2$) yields a slightly more stable η^6-X, coordinated through the aryl ring in good accordance with the experimental results. The difference is due to the electronic characteristics of the R substituents. The higher donating amino group creates an electron richer aryl with increased coordination ability, shifting the balance between the two possible coordination geometries. The small energy differences obtained for the relative stability of the two isomers of each complex (≤ 10 kJ mol^{-1}), however, suggest that the isolation of these species should be strongly dependent on experimental conditions such as the choice of the solvent. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thiophene; Aryl; Tricarbonylmanganese; Molecular orbital calculations; DFT; NLO

---

1. Introduction

Molecules with large π systems and, in particular, organometallic complexes have been extensively used in attempts to obtain materials with non-linear optical (NLO) properties. It has been shown that thiophene moieties contribute to the enhancement of such properties [1–15]. A recent report was published describing the synthesis, characterisation and NLO properties measurements of a family of tricarbonylmanganese complexes, $[(\eta^n\text{-X})Mn(CO)_3]^+$ (X = 1-(thiophenyl),2-(aryl)ethene), with different substituents on the aryl position *para* to the central ethene fragment (see Scheme 1) [16]. A η^5-X coordination through the thiophene ring is found for all the complexes, with the exception of the one corresponding to an amino-substituted aryl ($R = NMe_2$), where a η^6 coordinated aryl is observed.



Scheme 1.

In this work, ab initio [17] and DFT [18] calculations, complemented by an extended Hückel [19,20] orbital analysis are used to study the electronic structure of the $[(\eta^n\text{-X})Mn(CO)_3]^+$ complexes. Special emphasis is given to the (η-X)–Mn bonding and to the influence of the aryl substituent (R) on the competition between (η^5-X)–Mn thiophene and (η^6-X)–Mn aryl coordination. Two X π ligands, with R = OH and NH_2 substituents, respectively, are studied, corresponding to the complexes with X-ray structural characterisation [16].

E-mail address: veiros@ist.utl.pt (L.F. Veiros).

PII: S0022-328X(01)00814-2

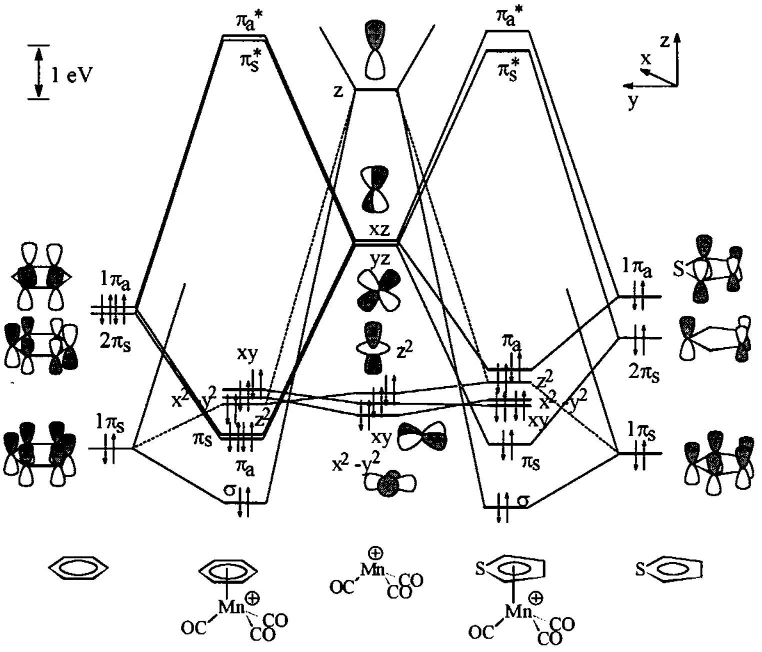


Fig. 1. Simplified MO diagram for the interaction between $[Mn(CO)_3]^+$ (centre) and C_6H_6 (left) or SC_4H_4 (right).

2. Results and discussion

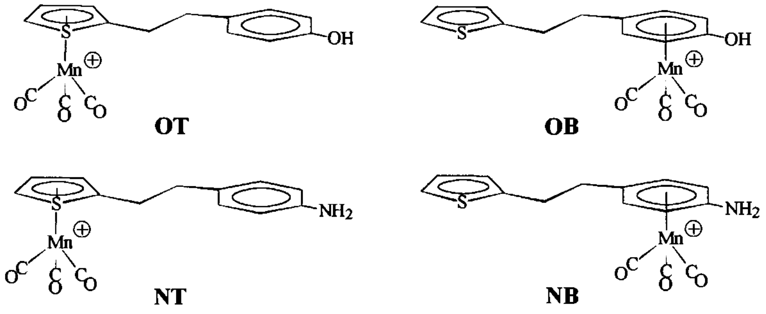
Although the bonding of the π-ligands to ML_3 fragments such as cyclopentadienyl in complex $[(\eta^5\text{-}C_5H_5)Mn(CO)_3]$ [21] is well known, a qualitative picture of the bonding of both a thiophene (η^5) and an aryl (η^6) to a $[Mn(CO)_3]^+$ fragment is useful as a starting point for a detailed analysis of the differences and similarities between those two coordination modes of π ligands (see Scheme 1), both of which lead to a 18-electron complex. Their interactions are represented in a schematic way, based on orbital symmetry considerations, in Fig. 1 which shows the molecular orbital (MO) diagram for two model complexes, $[(\eta^5\text{-}SC_4H_4)Mn(CO)_3]^+$ and $[(\eta^6\text{-}C_6H_6)Mn(CO)_3]^+$. A previously used [22–26] intuitive notation is adopted, 's' and 'a' meaning symmetric and antisymmetric with respect to the plane of a C_s symmetry.

Equivalent overall interactions are found for the two complexes in Fig. 1. In both cases the coordination of the π ligand consists of three interactions, one of σ and two of π symmetry (π_s and π_a). The first results from a three-orbital combination, namely the metal z and z^2 orbitals, empty and filled, respectively, and the ligand all symmetrical π orbital, ($1\pi_s$ in Fig. 1), the most stable of the ligand π set. Three MO result: one bonding, σ, filled and essentially composed by the ligand $1\pi_s$ orbital; the corresponding empty high-energy antibonding orbital, σ*, mostly metal z in character and not represented in Fig. 1; and a practically non-bonding orbital, filled at intermediate energy corresponding to metal z^2. The two π interactions result from the combination of the two metal d orbitals pointing towards the ligand (xz and yz in Fig. 1), both empty, with the ligand occupied π orbitals of appropriate symmetry, $1\pi_a$ and $2\pi_s$, respectively. They give rise to two occupied bonding orbitals, π_s and π_a, and their empty antibonding counterparts, π_s^* and π_a^*, which correspond to the group of lowest unoccupied molecular orbitals for both species. The other two metal d orbitals, xy and x^2-y^2 remain essentially non-bonding. The net result is the formation of three metal–ligand bonds which can formally be viewed as three two-electron donations from the ligand to the metal.

In spite of these similarities, some differences can be found in the bonding of a η^5-thiophene or a η^6-benzene to the metal, as represented in Fig. 1. In fact, a slightly stronger bond results from the thiophene coordination, as shown by the extended Hückel overlap population (OP) between interacting fragments, 0.636 for $(\eta^5\text{-}SC_4H_4)\text{–}[Mn(CO)_3]^+$ and 0.554 for $(\eta^6\text{-}C_6H_6)\text{–}[Mn(CO)_3]^+$, as well as by the corresponding binding energies (calculated as the difference between the energy of the complex and the sum of total energies of the separated fragments) of 318 and 218 kJ mol^{-1}. This is in good accordance with the experimentally observed preference of the tricarbonylmanganese moiety to coordinate thiophene rather than to the aryl ring [16]. The slightly stronger thiophene–metal bond is the result of two factors, a larger coordinating atom such as sulphur with more diffuse orbitals and the geometry of a five-membered ring, thiophene, instead of the six-membered aryl, both leading to a better overlap between interacting orbitals and consequently, to a stronger bond. The latter effect is seen better when comparing the OP between fragments for the benzene complex (see above) and its cyclopentadienyl analogue ($OP = 0.624$), showing again that a stronger bond is achieved for the five-membered ring. The same result was found previously in a study of $[(\eta^5\text{-Ring})Mn(CO)_3]$ complexes, comparing the cyclopentadienyl and indenyl species with the corresponding cyclohexadienyl and 1-hydronaphthalene complexes, which bind to the metal through five of the six carbon atoms in the ring [27].

Having established the nature of the bonding of the two π ligands (thiophene and benzene) to a $[Mn(CO)_3]^+$ fragment, the electronic structure of the $[(\eta^n\text{-}X)Mn(CO)_3]^+$ complexes, with both rings present in the X ligand (see Scheme 1) can be studied. The isolation and characterisation of a series of these complexes with different substituents (R) on the *para* carbon of the aryl ring, R = H, Me, NO_2, OMe and NMe_2, yielded η^5 thiophene coordinated X ligands in all cases, except for the amino-substituted X ($R = NMe_2$), where a η^6-X bonded through the aryl ring was found. The X-ray structural analysis reported for two of the complexes (R = OMe, NMe_2) confirmed the coordination geometry of the X π ligand, although a detailed structural analysis was prevented by the poor quality of the structures caused by anion disorder [16]. These species were thus chosen for the MO study described below, with hydrogen atoms replacing the methyl groups in the X ligand substituents (R = OH, NH_2), in order to save computational time. The two isomers of each $[(\eta^n\text{-}X)Mn(CO)_3]^+$ complex were considered (see Scheme 2), namely η^5-thiophene and η^6-aryl coordinated complexes with R = OH and $R = NH_2$-substituted X ligands, **OT**, **OB**, **NT** and **NB** in Scheme 2 and in the following discussion.

The optimised geometries of the four complexes are presented in Fig. 2 with the more relevant structural parameters. Given the poor quality of the structural data obtained for **OT** and **NB** real complexes, the validity of the theoretical model used (see Section 4) is better tested by comparing the geometries obtained with available experimental structures of related manganese carbonyl species with η^5-thiophene [28–31] and η^6-aryl coordinated [32–36] π ligands taken from the Cambridge Structural Database (CSD) [37].



Scheme 2.

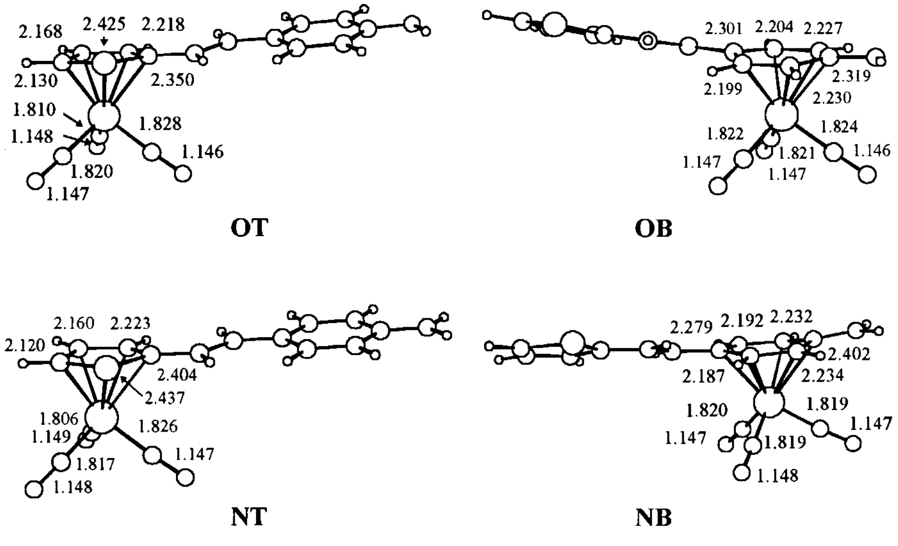


Fig. 2. Optimised structures (B3LYP/6-31G**) and more relevant bond distances (Å) for the $[(\eta^n\text{-}X)Mn(CO)_3]^+$ complexes for R = OH (top) and NH_2 (bottom), with η^5-thiophene (left) and η^6-aryl (right) coordination of the X ligands.

Table 1
Relative energies (kJ mol^{-1}), NPA charge distribution and carbonyl stretching frequencies (cm^{-1}) for the $[(\eta^n\text{-X})Mn(CO)_3]^+$ complexes

Complex	OT	OB	NT	NB
Relative energies (kJ mol^{-1})				
E	0	3	3	0
E_{slv}	1	0	10	0
NPA charge dist. [a]				
X	0.357	0.259	0.392	0.299
Mn	0.745	0.790	0.745	0.790
Carbonyls	−0.102	−0.049	−0.137	−0.089
ν(CO) (cm^{-1}) [a]				
Calc.	2034, 2076	2037, 2077	2027, 2071	2031, 2072
Exp. [16]	2016, 2064	–	–	2004, 2056

[a] See Section 4.

All the optimised structures correspond to piano stool geometries around the metal coordination sphere (see Fig. 2), typical of $[Mn(CO)_3]$ complexes with π ligands [37]. The (thiophene)–Mn bond distances obtained for **OT** and **NT** (Mn–S = 2.425, 2.437 Å and Mn–C = 2.120–2.404 Å) are in good agreement with the corresponding experimental ones (Mn–S = 2.307–2.330 Å and Mn–C = 2.130–2.304 Å), especially taking into account the fact that different complexes and coordination environments are compared [28–31]. The bonding in the metallic fragment, $[Mn(CO)_3]^+$, is also well described by the theoretical model used, as is shown by the comparison between the optimised distances (Mn–C(CO) = 1.806–1.828 Å, C–O = 1.146–1.149 Å) and the corresponding experimental ones (Mn–C(CO) = 1.743–1.832 Å, C–O = 1.115–1.173 Å). The same is observed for the aryl coordinated complexes, **OB** and **NB**, in which the calculated distances (Mn–C(aryl) = 2.187–2.402 Å, Mn–C = 1.819–1.824 Å and C–O = 1.146–1.148 Å) fit well in the experimental range (Mn–C(aryl) = 2.151–2.420 Å, Mn–C = 1.803–1.841 Å and C–O = 1.118–1.149 Å) [32–36].

Having established the performance of the theoretical model, a more detailed structural analysis of the complexes present in Fig. 2 can be carried out. In fact, a most striking feature of optimised structures (Fig. 2) is the similarity between the geometrical parameters obtained for each pair of equivalent isomers, i.e. the two complexes with thiophene coordination, **OT** and **NT**, and the two with aryl bonded X ligands, **OB** and **NB**. The mean and maximum absolute deviations on the bond lengths are 0.012 and 0.054 Å for **OT** and **NT** and 0.016 and 0.083 Å for **OB** and **NB**, respectively, giving an indication that equivalent overall bonding and consequently, approximate relative stability should be expected for the $[(\eta^n\text{-X})Mn(CO)_3]^+$ complexes with the two X ligands studied. This is confirmed by the relative energies for each pair of isomers presented in Table 1.

The relative stability shown in Table 1, (E) for each pair of isomers, is in complete agreement with the experimental isolated complexes, [16] i.e. a more stable η^5-thiophene coordination is observed for a hydroxyl-substituted X ligand and a η^6-aryl species is favoured when an amino group is present in the π ligand, X. However, the energy differences in each pair of isomers, **OT** and **OB**, on the one hand, and **NT** and **NB**, on the other, are very small (3 kJ mol^{-1}), being almost negligible. This may be caused, to some extent, by using model complexes in which the methyl groups on the X ligands substituents were replaced by hydrogen atoms (OH and NH_2 in the place of OMe and NMe_2).

In spite of being small, the energy differences obtained for each pair of isomers of the $[(\eta^n\text{-X})Mn(CO)_3]^+$ complexes are indicative of an electronic factor behind the observed preference for the aryl coordination of an amino-substituted X ligand. This may be traced to a second-order factor causing only subtle changes in electronic structure of the species, as should perhaps be expected, since the differences in the X ligands occur outside the Mn coordination sphere, not involving atoms directly bonded to the metal. A natural population analysis (NPA) was performed on the optimised complexes in order to obtain a better understanding of the electronic structure in those molecules and of the factors dictating the coordination preferences of the two studied X ligands.

The NPA results obtained for the four complexes studied are presented in Table 1 in terms of the charge distribution in each molecule, i.e. the charge on the X, π ligand, on the metal, Mn, and on the three carbonyl ligands, $(CO)_3$. The first result that emerges from Table 1 is the difference between thiophene and aryl coordination for both X ligands. In fact, a more effective charge transfer from X to the metallic moiety, $[Mn(CO)_3]$, is observed in the η^5-thiophene complexes. For the hydroxyl-substituted species (**OT** and **OB**), for example, the X coordinated ligand bears a more positive charge in **OT** (0.357) than in **OB** (0.259), leading to an electron richer metallic fragment in the first isomer. This is reflected by the metal charges, with a less positive manganese in **OT** ($C_{Mn} = 0.745$ vs 0.790 in **OB**), as well as by the electronic density in the carbonyl groups, more negative in the case of **OT** (−0.102 vs −0.049 in **OB**). The same pattern is found for the amino-substituted complexes, **NT** and **NB**. This means that a more effective electron donation from the π ligand to the metallic fragment is achieved when that ligand is coordinated through the thiophene ring, thus a stronger (η-X)–$[Mn(CO)_3]$ bond should result, in good accordance with both the experimental findings [16] and the conclusions drawn from Fig. 1 qualitative picture of the bonding (see above). On the other hand, one consequence of an enhanced electron donation from X is the increase in the metal to carbonyl backdonation, as shown by the carbonyl charges, yielding the well-known weakening of the C–O bond, which is reflected in the corresponding stretching frequencies. In fact, in the calculated ν(C–O) frequencies for each pair of isomers (see Table 1) a decrease of 1–4 cm^{-1} is found going from the aryl bonded to the thiophene coordinated species, showing that a slightly weaker C–O bond is present in the latter species. The small differences obtained for the frequencies are consistent with a weak, second-order effect resulting from changes outside the metal coordination sphere corroborating the almost equivalent stability found in each pair of isomers. It should be mentioned that the frequencies calculated for **OT** and **NB** are in very good agreement with the experimental ones [16], with 0.9 and 1.3% mean and maximum absolute deviations, respectively.

Although a first observation of the charges in Table 1 leads to the conclusion that a slightly stronger (η-X)–Mn bond should be achieved for a thiophene coordination, the fact is that both the calculated relative stability and the experimental findings show that η^6-aryl complexes are favoured for amino-substituted X ligands (**NB**). Thus, in this case, some additional effect is expected, shifting the balance towards the observed aryl bonding. The results on the two aryl bonded complexes with different X ligands (**OB** and **NB**) have to be compared in order to explain the preferred coordination mode.

A comparison between the charge distribution on **OB** and **NB** shows that in the latter species there is a stronger electron donation from the X ligand to the $[Mn(CO)_3]$ moiety. In fact, **NB** has a slightly more positive X (0.299 vs 0.259 for **OB**) and consequently, an electronically richer metallic fragment, the difference being found on the carbonyl ligands (−0.089 for **NB** and −0.049 for **OB**). This is also shown by the corresponding carbonyl stretching frequencies 5–6 cm^{-1} smaller in **NB**. Thus, a more effective X–$[Mn(CO)_3]$ donation exists in the amino-substituted complex leading to a stronger metal to carbonyl backdonation. The same pattern is found when comparing the two thiophene-bonded complexes and is a consequence of the electronic characteristics of the two substituents, NH_2 being a better electron donor than OH.

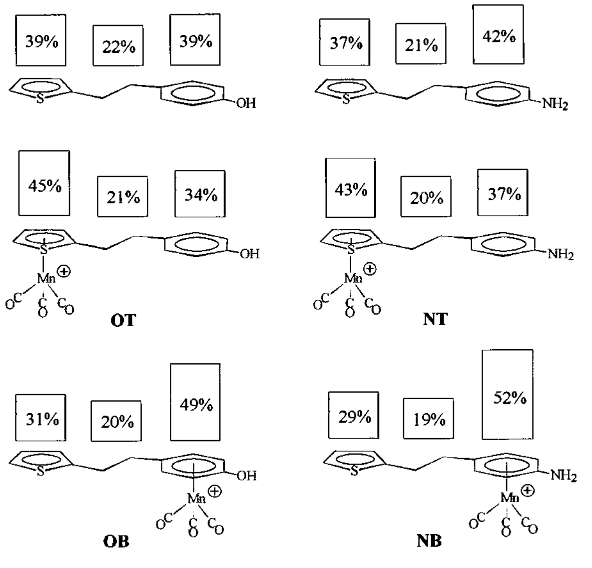


Fig. 3. NPA charge distribution among the thiophene ring, the C_2 connecting chain and the aryl ring for the free and coordinated X ligands.

A deeper insight of the X ligands electronic structure as a function of the substituent can be gained from Fig. 3, in which the charge distribution along X is depicted for the four complexes studied $[(\eta^n\text{-X})Mn(CO)_3]^+$ and the two free ligands, in terms of the fraction of the ligands electronic density present in the thiophene ring, the aryl ring and the connecting C_2 chain in each case. Two major features emerge from Fig. 3. On one hand, there is a displacement of X electronic density towards the coordinated ring, in all cases, and on the other, the amino-substituted ligands reveal a shift of the charge to the aryl ring, when compared with their hydroxyl-substituted equivalents. In fact, for **OT** and **NT** the thiophene ring has the greater portion of the ligands charge, but it falls from 45% in the first complex to 43% in the second. The equivalent situation is found for **OB** and **NB**, with 49 and 52% X electronic density in the aryl ring, respectively. The substituent influence on X charge distribution is, perhaps, better seen in the free ligands, where an even distribution between the two rings is found for R = OH (39% in each) and an electronically richer aryl exists for R = NH_2, with 42% of the electron density versus 37% in the thiophene ring.

Although well known, the differences between the donating capabilities of the two substituents (OH and NH_2) may be further corroborated by a structural analysis, comparing the free and the coordinated ligand, X. In all cases, a shorter C(aryl)–R bond is observed in the coordinated ligand, when compared with the free one, indicating that the electronic density donated to the metallic fragment upon coordination is compensated by π donation from substituent (R) to the remaining of the molecule, as should be expected for electron donors such as OH and NH_2. However, this effect is more pronounced for R = NH_2, than for R = OH. For the former, a 4% decrease in the C(aryl)–NH_2 bond length is found when going from the free X ligand to **NB**, for example, while the C(aryl)–OH bond in **OB** is only 2% shorter than in the free ligand. The π donation from NH_2 to the rest of the coordinated X ligand is also reflected by the difference in the N atom hybridisation for a free and a coordinated X. In fact, a pyramidalised, sp_3 N is observed in the free ligand, the sum of the three bond angles around this atom being

228°; on the other hand, a planar sp_2 N atom can be found in **NB**, the three bond angles around N adding up 360°.

Another interesting aspect, related to the charge distribution in X, is the deviation from planarity observed in these ligands in the complexes studied. It can be measured by the torsion angle between the two rings (α), an increasingly planar X corresponding to α values decreasing to zero. Greater planarity deviations are consistently found in the aryl coordinated species ($\alpha_{\mathbf{OB}} = 18°$, $\alpha_{\mathbf{NB}} = 19°$), when compared with the η^5-thiophene complexes ($\alpha_{\mathbf{OT}} = 10°$, $\alpha_{\mathbf{NT}} = 6°$), in good accordance with the experimental findings for **OT** and **NB** real complexes [16]. The above discussion on the electronic structure of these species shows that charge flows from the R donor group, in the X ligand, to an acceptor metallic fragment, $[Mn(CO)_3]$, in all cases. For a thiophene coordinated X, these two moieties are present at opposite ends of the X ligand. In this situation, the entire π system of X must be involved in the charge transfer and, hence, a more planar ligand results.

The differences in the charge distribution in X ligands as a function of the R substituent, shown in Fig. 3 and discussed above, can help in understanding the preference for the η^6-aryl coordination of an amino-substituted X, reflected by relative energies (E) given in Table 1 and experimentally observed. Thus, for R = NH_2 an increase of the electronic density on the aryl ring occurs, enhancing its coordination ability and shifting the tight balance between a η^5-thiophene and a η^6-aryl bonding towards the latter.

It should be noticed that, given the small differences in stability (see Table 1) and in the electronic structure of the studied species, the isolation of any of the two $[(\eta^n\text{-X})Mn(CO)_3]^+$ isomers for each X ligand should be, in principle, possible, depending on the experimental conditions such as the solvent choice, for example. The effect of the experimentally used solvent (dichloromethane) was taken into account by means of energy calculations using a cavity model (see Section 4) and the optimised geometries. The resulting relative energies (E_{slv}) are presented in Table 1, and show that the stability of the aryl bonded complex is favoured by dichloromethane in both cases, but with different degrees for the two X ligands. Thus, a comparatively small solvent effect is found for the hydroxyl-substituted complexes, decreasing the stability difference between the two isomers, **OT** and **OB**, and leading to two practically isoenergetic species (differing by only 1 kJ mol^{-1}). On the other hand, a more important solvent effect is found for the amino-substituted complexes; the result is an increased stability difference between two isomers, **NB** becoming the more stable one by 10 kJ mol^{-1}. These results suggest that the use of dichoromethane as solvent clearly favours the η^6-aryl coordination for an amino-substituted X ligand, corroborating the isolation of such a species when R = NMe_2 [16], and revealing the importance of the experimental conditions on the obtained final product.

3. Conclusions

The coordination mode of the X π ligand, X = 1-(thiophenyl),2-(aryl)ethene, in the $[(\eta^n\text{-X})Mn(CO)_3]^+$ complexes depends on the electronic characteristics of the substituent (R) present on the aryl *para* carbon, with respect to the ethene. For R = OH, a η^5-thiophene complex results, while for the better electron donor NH_2 a η^6-aryl coordination is preferred. The advantages of a better X–M overlap resulting from the thiophene five-membered ring geometry and larger sulphur atom are overtaken by an electronically richer aryl with enhanced coordination ability, when R = NH_2.

The small differences obtained for the relative stability and the similarities between the electronic structures of each pair of isomers, suggest that the isolation of a complex with any of the two possible X coordinating modes should be possible for both X ligands, depending on the experimental conditions.

4. Computational details

The geometry optimisations were accomplished by means of ab initio and DFT calculations performed with the GAUSSIAN 98 program [38]. The B3LYP hybrid functional with a standard 6-31G** basis set [39], was used in all optimisations. This functional includes a mixture of Hartree–Fock [17] exchange with DFT [18] exchange-correlation, given by Becke's three parameter functional [40] with the Lee, Yang and Parr correlation functional, which includes both local and non-local terms [41,42]. All the optimised geometries are the result of full optimisations without any symmetry constraints. The stationary points were confirmed by frequency calculations and the energies were zero point corrected. The calculated frequencies presented along the text were scaled by a 0.9613 factor [43]. A natural population analysis (NPA) [44] was performed in order to obtain the charge distribution on the optimised species. A static isodensity surface polarised continuum model [45] was used to account for the solvent (dichloromethane) effect on the relative stability of the different species.

The extended Hückel calculations [19,20] were done with the CACAO program [46] and modified H_{ij} values were used [47]. The basis set for the metal atoms consisted of ns, np and $(n-1)$d orbitals. The s and p orbitals were described by single Slater-type wave functions and the d orbitals were taken as contracted linear combinations of two Slater-type wave functions. Only s and p orbitals were considered for S. The parameters used for Mn were the following (H_{ii} (eV), ζ): 4s −9.880, 1.800; 4p −5.450, 1.800; 3d −12.530, 5.150, 1.900 (ζ_2), 0.5311 (C_1), 0.6479 (C_2). Standard parameters were used for other atoms. Calculations were performed on models based on the optimised geometries with idealised maximum symmetry and the following distances (Å): Mn–C (aryl) 2.20, Mn–C (thiophene) 2.13, Mn–C (CO) 1.80, Mn–S 2.46, C–O 1.15, C–C 1.40, S–C 1.75, C–H 1.08; and angle: X–Mn–CO 120°.

Acknowledgements

Praxis XXI is acknowledged for partial funding of this work.

References

[1] I.D.L. Albert, T.J. Marks, M.A. Ratner, J. Am. Chem. Soc. 119 (1997) 6575.

[2] M. Szalewski, P.R. Thomas, A. Thornton, D. Bloor, G.H. Cross, J.M. Cole, J.A.K. Howard, M. Malagoli, F. Meyers, J.-L. Brédas, W. Wenseleers, E. Goovaerts, J. Am. Chem. Soc. 119 (1997) 3144.

[3] Q.T. Whang, J.M. Tour, J. Am. Chem. Soc. 119 (1997) 5065.

[4] D.D. Graf, R.G. Duan, J.P. Campbell, L.L. Miller, K.R. Mann, J. Am. Chem. Soc. 119 (1997) 5888.

[5] N.J. Long, Angew. Chem. Int. Ed. Engl. 34 (1995) 21.

[6] M.G. Hutchings, I. Ferguson, D.J. McGeein, J.O. Morley, J. Zyss, I. Ledoux, J. Chem. Soc. Perkin Trans. 2 (1995) 171.

[7] K.J. Drost, V.P. Rao, A.K.-Y. Jen, J. Chem. Soc. Chem. Commun. (1994) 369.

[8] V.P. Rao, Y.M. Cai, A.K.-Y. Jen, J. Chem. Soc. Chem. Commun. (1994) 1689.

[9] V.P. Rao, A.K.-Y. Jen, K.Y. Wong, K.J. Drost, J. Chem. Soc. Chem. Commun. (1993) 1118.

[10] V.P. Rao, A.K.-Y. Jen, K.Y. Wong, K.J. Drost, Tetrahedron Lett. 34 (1993) 1747.

[11] A.K.-Y. Jen, V.P. Rao, K.Y. Wong, K.J. Drost, J. Chem. Soc. Chem. Commun. (1993) 90.

[12] S.A. Jenekhe, W.C. Chen, S. Lo, S.R. Flom, Appl. Phys. Lett. 57 (1990) 126.

[13] Y. Wei, R. Hariharan, R. Bakthavatchalam, J. Chem. Soc. Chem. Commun. (1990) 1161.

[14] J. Lewis, N.J. Long, P. Raithby, G.P. Shields, W.Y. Wong, M. Younus, J. Chem. Soc. Dalton Trans. (1997) 4283.

[15] I.-Y. Wu, J.T. Lin, J. Luo, C.-S. Li, C. Tsai, Y.S. Wen, C.-C. Hsu, F.-F. Yeh, S. Liou, Organometallics 17 (1997) 2188.

[16] I.S. Lee, H. Seo, Y.K. Chung, Organometallics 18 (1999) 1091 (see also p. 5194).

[17] W.J. Hehre, L. Radom, P.v.R. Schleyer, J.A. Pople, Ab Initio Molecular Orbital Theory, Wiley, New York, 1986.

[18] R.G. Parr, W. Yang, Density Functional Theory of Atoms and Molecules, Oxford University Press, New York, 1989.

[19] R. Hoffmann, J. Chem. Phys. 39 (1963) 1397.

[20] R. Hoffmann, W.N. Lipscomb, J. Chem. Phys. 36 (1962) 2179.

[21] T.A. Albright, J.K. Burdett, M.H. Whangbo, Orbital Interactions in Chemistry, Wiley, New York, 1985, pp. 384–385.

[22] C. Bonifaci, A. Ceccon, S. Santi, C. Mealli, R.W. Zoellner, Inorg. Chim. Acta 240 (1995) 541.

[23] M.J. Calhorda, C.A. Gamelas, I.S. Gonçalves, E. Herdtweck, C.C. Romão, L.F. Veiros, Organometallics 17 (1998) 2597.

[24] M.J. Calhorda, L.F. Veiros, Coord. Chem. Rev. 37 (1999) 185–185.

[25] L.F. Veiros, J. Organomet. Chem. 587 (1999) 221.

[26] L.F. Veiros, Organometallics 19 (1999) 5549.

[27] L.F. Veiros, Organometallics 19 (2000) 3127.

[28] S.S. Lee, T.-Y. Lee, J.E. Lee, I.-S. Lee, Y.K. Chung, M.S. Lah, Organometallics 15 (1996) 3664.

[29] T.A. Waldbach, P.H. van Rooyen, S. Lotz, Angew. Chem. Int. Ed. Engl. 32 (1996) 710.

[30] T.A. Waldbach, P.H. van Rooyen, S. Lotz, Organometallics 12 (1993) 4250.

[31] A.J. Deeming, M.K. Shinhmar, A.J. Arce, Y. De Sanctis, J. Chem. Soc. Dalton Trans. (1999) 1153.

[32] P.H. van Rooyen, L. Geer, S. Lotz, Acta Crystallogr. Sect. C 46 (1990) 1432.

[33] E. Jeong, Y.K. Chung, J. Organomet. Chem. 434 (1992) 225.

[34] A.J. Pearson, P.Y. Zhu, W.J. Youngs, J.D. Bradshaw, D.B. McConville, J. Am. Chem. Soc. 115 (1993) 10 376.

[35] S. Sun, G.B. Carpenter, D.A. Sweigart, J. Organomet. Chem. 511 (1996) 257.

[36] J.D. Jackson, S.J. Villa, D.S. Bacon, R.D. Pike, G.B. Carpenter, Organometallics 13 (1994) 3972.

[37] F.H. Allen, J.E. Davies, J.J. Galloy, O. Johnson, O. Kennard, C.F. Macrae, D.G. Watson, J. Chem. Inf. Comput. Sci. 31 (1991) 204.

[38] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Rob, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, GAUSSIAN 98, Revision A.7, Gaussian Inc., Pittsburgh PA, 1998.

[39] (a) R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724;
(b) W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257;
(c) P.C. Hariharan, J.A. Pople, Mol. Phys. 27 (1974) 209;
(d) M.S. Gordon, Chem. Phys. Lett. 76 (1980) 163;
(e) P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.

[40] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[41] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.

[42] B. Miehlich, A. Savin, H. Stoll, H. Preuss, Chem. Phys. Lett. 157 (1988) 200.

[43] J.B. Foresman, Æ. Frisch, Exploring Chemistry with Electronic Structure Methods, 2nd ed., Gaussian Inc, Pittsburgh, PA, 1996 p. 64.

[44] (a) J.E. Carpenter, F. Weinhold, J. Mol. Struct. (Theochem) 169 (1988) 41;
(b) J.E. Carpenter, PhD thesis, University of Wisconsin, Madison, WI, 1987;
(c) J.P. Foster, F. Weinhold, J. Am. Chem. Soc. 102 (1980) 7211;
(d) A.E. Reed, F. Weinhold, J. Chem. Phys. 78 (1983) 4066;
(e) A.E. Reed, F. Weinhold, J. Chem. Phys. 78 (1983) 1736;
(f) A.E. Reed, R.B. Weinstock, F. Weinhold, J. Chem. Phys. 83 (1985) 735;
(g) A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899;

(h) F. Weinhold, J.E. Carpenter, The Structure of Small Molecules and Ions, Plenum, New York, 1988 (227pp.).

[45] J.B. Foresman, T.A. Keith, K.B. Wiberg, J. Snoonian, M.J. Frisch, J. Phys. Chem. 100 (1996) 16 098.

[46] C. Mealli, D.M. Proserpio, J. Chem. Educ. 67 (1990) 39.

[47] J.H. Ammeter, H.-J. Bürgi, J.C. Thibeault, R. Hoffmann, J. Am. Chem. Soc. 100 (1978) 3686.