Journal of Organometallic Chemistry, 332 (1987) 153–164
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Study of the interaction between iron(0) and carbon dioxide, carbonyl sulphide and carbon disulphide: "ab initio" calculations on the model compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, and $Fe(PH_3)_4(\eta^2\text{-}CO_2)$

M. Rosi, A. Sgamellotti, F. Tarantelli

Dipartimento di Chimica, Università di Perugia, Via Elce di Sotto 8, I-06100 Perugia (Italy)

and C. Floriani

I.C.M.A., Université de Lausanne, Place du Château 3, CH-1005 Lausanne (Switzerland)

(Received February 17th, 1987)

Abstract

"Ab initio" calculations have been performed on the model systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ in order to investigate the nature and energetics of the interaction between iron and CO_2, COS, CS_2. The results suggest that the main bonding interaction between the fragment $Fe(CO)_2(PH_3)_2$ and the unsaturated molecule is the π-back-donation from the transition metal to the π-acceptor ligand and that the strength of the coordination bond increases in the order $CO_2 < COS < CS_2$. Partial geometry optimizations obtained by gradient calculations show that carbonyl sulphide prefers the η^2-C,S rather than the η^2-C,O coordination mode because of the increased π-back-donation.

The study of the system $Fe(PH_3)_4(\eta^2\text{-}CO_2)$ reveals that the presence of donor ligands, such as phosphine, by increasing the electronic population at the metal centre, enhances the π-back-donation and thus the strength of the interaction.

Introduction

Activation of carbon dioxide, which is potentially the most abundant source of C_1 compounds may be reasonably expected to be brought about by transition metal catalysis. Despite considerable research, however, formation of carbon dioxide complexes is quite rare, and their chemistry is limited to a small number of compounds [1–8]. Although CS_2 is structurally very similar to CO_2 its behaviour

0022-328X/87/$03.50

towards metal centres is so different that it would be interesting to study the interaction of the two compounds with the same metallic fragment in order to elucidate the origins of this difference, and this was the objective of the present work. The species COS, which is expected to have mixed properties, is also examined. Recently two theoretical studies on the interaction of carbon dioxide and carbon disulphide with a nickel fragment have appeared [10,11] and both imply that the side-on bonding interaction is the most favorable. Moreover, an accurate analysis of such a bonding mode led to the conclusion that, contrary to what is expected for the classic Chatt-Dewar-Duncanson model [12], the predominant role is played by π-back-donation, and σ-donative interaction may be irrelevant or absent.

To our knowledge, no "ab initio" MO investigations have been reported on transition metal complexes with carbon disulphide and carbonyl sulphide. In this paper we investigate the relative stabilities of the three model systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ by "ab initio" MO calculations. Such a comparison should allow evaluation of the role of the heteroatom (O or S) in forming stable complexes. The most closely related known complexes that can be found in the literature are $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$ [13] and $Fe(PMe_3)_4(CO_2)$ [3]. The existence of the latter is taken as justification for our use of $Fe(PH_3)_4(\eta^2\text{-}CO_2)$, as a model for investigating the effects of ligand substitution in the case of coordination of CO_2.

Computational details

Basis sets

Two Gaussian basis sets, hereafter denoted as I and II, were employed throughout this work. In basis I, the functions for iron were derived from Huzinaga's MINI-4 basis [14], by splitting the outermost *s* and *d* functions. The MINI-1 basis [15,16] was used for the phosphorus atoms and the carbonyl groups, and a (2*s*) contraction [15] of Van Duijneveldt's (4*s*) primitive set [17] was used for the phosphine hydrogens. For the component atoms of carbon dioxide, carbonyl sulphide, and carbon disulphide, Dunning's basis set [18,19] of double zeta quality was employed. All geometry optimizations described in this work were conducted using this basis. Subsequent single point SCF calculations at the optimized geometries were performed with the more extended basis II. Here the *s*,*p* basis for iron was taken from the (12*s*6*p*4*d*) set of ref. 20, with the addition of two basis functions to describe the 4*p* orbital [21], while the Fe *d* basis was the reoptimized (5*d*) set of ref. 22, contracted (4/1). This leads to an (11*s*8*p*5*d*) primitive basis for iron, contracted (8*s*6*p*2*d*). A double zeta expansion was used for all ligand atoms, with a (4*s*/2*s*) basis for H [18], a (9*s*5*p*/4*s*2*p*) contraction for carbon and oxygen [18], and an (11*s*7*p*/6*s*4*p*) contraction for phosphorus and sulfur [19].

The reliability of such basis sets was confirmed in an earlier study of the interaction between iron and formaldehyde [23]. In particular, the basis set superposition error was evaluated as described by Boys and Bernardi [24] and found to be acceptably small (3.9 kcal mol^{-1} with basis I, 4.6 kcal mol^{-1} with basis II).

MO method

"Ab initio" spin restricted Hartree-Fock SCF gradient calculations were used in partial geometry optimizations of the four complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$,

$Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, ($\eta^2$-C,O bonded and η^2-C,S bonded) and $Fe(PH_3)_4(\eta^2\text{-}CO_2)$ and in deriving estimates of the binding energies of all the complexes with respect to free CXY (with X, Y = O and/or S) and fragment species.

All computations were performed using the GAMESS program package [25], implemented on the cluster of FPS-164 processors at the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome).

Geometries and geometry optimization

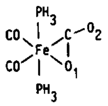
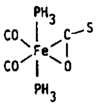
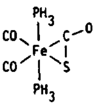
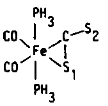
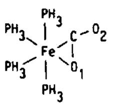
In all the calculations described here we confined our attention to geometries involving side-on coordination of the CXY molecule. The study of Morokuma et al. [10] together with experimental results [26] has shown that the end-on coordination mode is preferred only when the metal atom has a considerable positive charge. On the other hand, C-coordination has been observed only in the compounds Co(n-Pr-salen)K(CO_2)(THF) [2], Rh(diars)$_2$Cl(CO_2) [8], and it is probably present in Ir(dmpe)$_2$Cl(CO_2) [27]. Hoffmann et al. [11] suggest that this coordination mode occurs when "the metal atom is electronically saturated by its coligands and the fragment has a free coordination site". For the iron(0) unsaturated fragments $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$, with two potentially coordination sites free, only the side-on coordination mode has been considered.

Partially optimized structures of the complexes under investigation are shown in Table 1. All the compounds can be viewed as either a distorted trigonal bipyramid with a 5-coordinate iron atom, or a distorted octahedron with a 6-coordinate iron atom, depending on whether the unsaturated ligand CXY is considered to be monodentate or bidentate. The iron atom is bonded to two mutually *trans* phosphines in axial sites and to two carbonyls (or two phosphines) and CXY in equatorial sites. The geometries of the $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$ fragments were taken from ref. 23 and kept frozen during the optimizations.

All the geometrical parameters involved in the interaction Fe–CO_2 in the compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and $Fe(PH_3)_4(\eta^2\text{-}CO_2)$ as well as those rela-

Table 1

Optimized geometries of the systems under investigation. Bond lengths in Å, angles in °. $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ geometry has been deduced from the experimental structure of $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$ (See text)

									
Fe-C	1.842	Fe-C	1.852	Fe-C	1.857	Fe-C	1.983	Fe-C	1.792
Fe-O_1	2.124	Fe-O	2.101	Fe-S	2.457	Fe-S_1	2.335	Fe-O_1	2.188
C-O_1	1.247	C-O	1.230	C-S	1.767	C-S_1	1.676	C-O_1	1.258
C-O_2	1.217	C-S	1.689	C-O	1.202	C-S_2	1.615	C-O_2	1.234
$\angle O_1$-C-O_2	140.5	$\angle$O-C-S	139.0	$\angle$S-C-O	138.0	$\angle S_1$-C-S_2	138.9	$\angle O_1$-C-O_2	137.3
$\angle$C-Fe-CO	96.0	$\angle$C-Fe-CO	96.9	$\angle$C-Fe-CO	94.3	$\angle$C-Fe-CO	92.3	$\angle$C-Fe-PH_3	95.4

tive to the interaction Fe–COS (with the carbonyl sulphide η^2-C,O and η^2-C,S iron bonded) were optimized. The reliability of such calculations was checked in an earlier study on the compound $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ [23] by comparing the experimental and optimized structures. In the compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and $Fe(PH_3)_4(\eta^2\text{-}CO_2)$, the calculated Fe–C bond lengths (1.842 Å and 1.792 Å, respectively) are shorter than the corresponding Fe–O bond lengths (2.124 Å and 2.188 Å, respectively) and this feature is in agreement with the experimental structure of the known carbon dioxide-transition metal complexes, where CO_2 is η^2-C,O bonded to the metal. Thus the M–C and M–O bond lengths are 1.84 and 1.99 Å in $[Ni(PCy_3)_2(\eta^2\text{-}CO_2), 0.75\ (C_7H_8)]$ [4]; 2.112 and 2.160 Å in $[(C_5H_5)_2Mo(\eta^2\text{-}CO_2)]$ [5]; 2.144 and 2.173 Å in $[Nb(\eta\text{-}C_5H_4Me)_2(CH_2SiMe_3)(\eta^2\text{-}CO_2)]$ [7]; 2.105 and 2.147 Å in $[Mo(PMe_3)_3(CNPr^i)(\eta^2\text{-}CO_2)_2]$ [6]. The C–O bond lengths are calculated to be 1.247 Å in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and 1.258 Å in $Fe(PH_3)_4(\eta^2\text{-}CO_2)$, and these values are comparable with those observed in the complexes with CO_2, which lie between 1.22 and 1.29 Å [4–7]. The angles OCO are calculated to be 140.5° in the dicarbonyldiphosphine compound and 137.3° in the tetrakis(phosphine) compound, and these values are slightly greater than the experimental ones, which are around 133° [4–7], but they are very close to the optimized value for the model system $Ni(PH_3)_2(\eta^2\text{-}CO_2)$, which is 139° [10]. The bond angles and distances relative to the interaction Fe–CS_2 in the complex $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ were taken directly from the experimental structure of $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$ [13]. The experimental geometries of CO_2, COS, and CS_2 were used for the the free molecules [28].

In considering the electronic structures of the isolated fragments $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$, we took the geometries to be equal to those in the complexes. Dissociation to these fragments may lead to either singlet or triplet products. In a previous study [23], configuration interaction calculations on the complex $Fe(CO)_4(\eta^2\text{-}CH_2O)$ led us to suggest that fragmentation of that complex leads to singlet products, given the $S_0 \rightarrow T_1$ value of 71.9 kcal mol^{-1} for free formaldehyde [28]. The $S_0 \rightarrow T_1$ value for free carbon disulphide is 74.7 kcal mol^{-1} [28], and that for free carbon dioxide is 113 kcal mol^{-1} [29]. We can thus assume with some confidence that fragmentation of the complexes under examination will lead to singlet products, though the structure of the coordinated CS_2 in $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$ has been related to the $^3A_2$ excited state geometry of CS_2 [13].

Results and discussion

Study of the interaction between $Fe(CO)_2(PH_3)_2$ and CO_2, COS, CS_2

The total SCF energies of the complexes and fragments under investigation, together with estimates of the interaction energies, are listed in Table 2. We start our analysis with the complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$ (η^2-C,S bonded), and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$. Bond formation between iron and heterocumulene can result either from a substitution reaction (eq. 1), or from an

$$Fe(CO)_2(PH_3)_2L + CXY \rightarrow Fe(CO)_2(PH_3)_2(\eta^2\text{-}CXY) + L \qquad (1)$$

addition to a "hot" metallic fragment (eq. 3) thermally or photochemically generated in a previous stage (eq. 2).

$$Fe(CO)_2(PH_3)_2L \xrightarrow{h\nu \text{ or } \Delta} \text{“}Fe(CO)_2(PH_3)_2\text{”} + L \qquad (2)$$

$$\text{“}Fe(CO)_2(PH_3)_2\text{”} + CXY \rightarrow Fe(CO)_2(PH_3)_2(\eta^2\text{-}CXY) \qquad (3)$$

The binding (or interaction) energy between the metal and the heterocumulene is that related to reaction 3. Since we use frozen-geometry fragments and partially optimized complex geometries, we expect our calculated interaction energies to overestimate the true fragmentation energies of the complexes, but this should not unduly affect our comparative analysis.

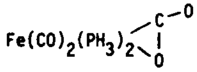
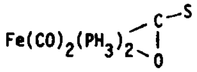
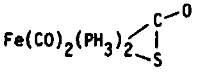
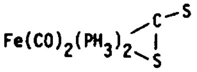
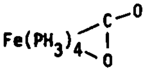
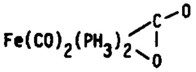
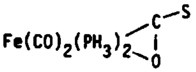
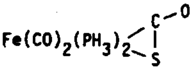
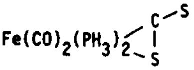
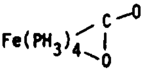
The binding energies are calculated to be -26.2, -35.8, -39.1 kcal mol^{-1} with basis I, and -19.5, -44.7, -50.9 kcal mol^{-1} with basis II, for the three complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$ (η^2-C,S bonded), $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, respectively (Table 2). To attempt an interpretation of these data we must first analyse the bond structure of the complexes as revealed by our calculations. A useful way of understanding the nature of the metal–CXY bond is provided by the correlation of the molecular orbitals of the complex with those of the fragments. Figure 1 shows such a correlation diagram of the orbitals of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ with those of the singlet fragments, only the main correlations being shown. To show the effects of CO_2 distortion upon complex formation, the orbital energy levels of free CO_2 at both the equilibrium geometry and for a C_s geometry of the complex are shown in the Fig. 1. It can be seen that the orbitals mainly involved in the iron–carbon dioxide bonding are the $37a'$, $38a'$, and $39a'$ orbitals, while $17a''$ is a non-bonding orbital localized on the CO_2. The $37a'$ and $38a'$ molecular orbitals originate from the interaction of the filled orbitals $Fe(CO)_2(PH_3)_2\text{-}19a_1$ and $CO_2\text{-}9a'(1\pi_g)$. This is a four electron destabilizing interaction. Effective bonding, therefore, is concentrated in the $39a'$ orbital, which is the bonding combination of $Fe(CO)_2(PH_3)_2\text{-}11b_2$ (hereafter denoted by d_π), and the virtual orbital of CO_2, $10a'(2\pi_u)$ (hereafter denoted by $\pi^\star$). The former orbital is predominantly Fe-d_{xy} in character (the Fe–CO_2 moiety lies in the xy plane). Thus the main bonding interaction is the π-back-donation from the metal atom to the unsaturated ligand. Such a result seems to support further the conclusion that the coordination of a $\rangle C{=}X$ functionality to a metal site has to be regarded as the consequence of an efficient π-back-donation, rather than as in a Chatt–Dewar–Duncanson model, in which the L → M σ-donation also makes a significant contribution. Figure 1 shows also that the CO_2 distortion upon coordination lowers the $\pi^\star$ orbital energy and reduces the gap between this orbital and the fragment d_π orbital. The distortion of CO_2 therefore implies an increased π-back-donation.

The other complexes show the same bonding picture: the main bonding orbital is always the overlap between the $Fe(CO)_2(PH_3)_2\text{-}d_\pi$ and the ligand-$\pi^\star$ orbitals. Thus, the main bonding interaction is the π-back-donation from the metal atom to the unsaturated ligand.

The interaction energy increases in the order $CO_2 < COS < CS_2$, suggesting an increase in the π-back-donation. This is confirmed by Mulliken population analysis, shown in Table 3 for basis II calculations, which assigns a negative charge of 0.52, 0.56, and 0.64 to CO_2, COS, and CS_2, respectively. This trend in the π-back-donation is in agreement with the $\pi^\star$ orbital energies of the distorted ligand, shown in

Table 2

Total SCF energies (hartree) and binding energies (kcal/mol) of the analysed systems

COMPLEX	BASIS I	BASIS II
	-2350.4204	-2359.6477
	-2673.0489	-2682.2803
	-2673.0567	-2682.3087
	-2995.6767	-3004.9334
	-2808.0448	-2819.0490
FRAGMENT		
$Fe(CO)_2(PH_3)_2$	-2162.8254	-2172.0633
$Fe(PH_3)_4$	-2620.3905	-2631.3982
CO_2	-187.5533	-187.5533
COS	-510.1742	-510.1742
CS_2	-832.7890	-832.7890
BINDING ENERGIES		
	-26.2	-19.5
	-30.9	-26.9
	-35.8	-44.7
	-39.1	-50.9
	-63.4	-61.2

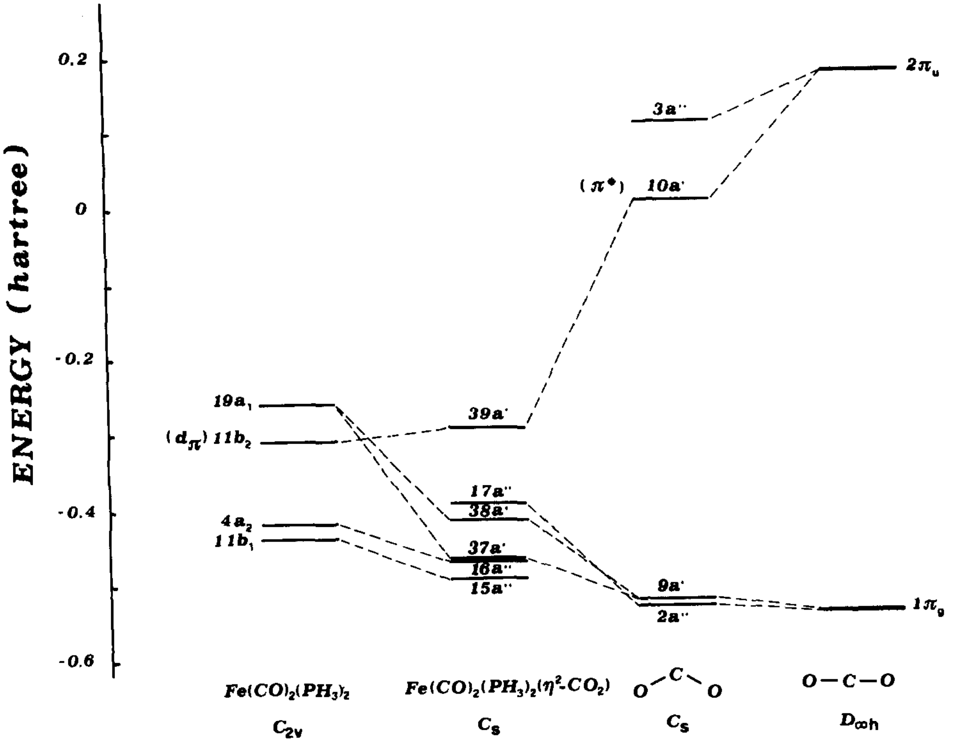


Fig. 1. Molecular orbital correlation diagram of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$.

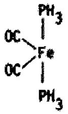
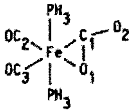
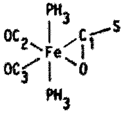
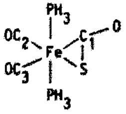
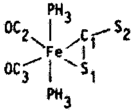
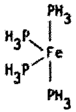
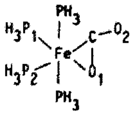
Table 3, which are 0.0055, −0.0137, and −0.0187 au, and with the experimental electron affinities of the CXY ligand, which are −0.6, 0.46, and 1.0 eV, for CO_2, COS, and CS_2, respectively [1a].

We notice that the calculated interaction energy is greater for basis II than for basis I, for $Fe(CO)_2(PH_3)_2(\eta^2\text{-COS})$ (η^2-C,S bonded) and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, but the order is reversed for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$. The greater strength of the Fe–CXY bond in the carbonyl sulphide and carbon disulphide compounds can be explained by the better description of the iron atom achieved with basis II. The resulting increased electron density at the metal centre must imply a more pronounced back-donation towards the unsaturated ligands. On the other hand, since basis II also provides a better description of the carbonyl groups, the weaker Fe–CO_2 bond could be due to a competition towards π-back-donation between CO_2 and CO, almost absent in basis I calculations because of the different description of the orbitals of these ligands.

A common feature of the analysed compounds is the strongly distorted geometry of the coordinated CXY ligand. As previously mentioned, this can be seen from the π^* orbital energies of the ligands, which are 0.1723, 0.1084, and 0.0557 au for CO_2, COS, and CS_2 in the equilibrium geometries and become 0.0055, −0.0137, and −0.0187 au for the ligands in the distorted geometries. The deformation of the ligands, therefore, lowers the π^* orbital energy and reduces the gap between this orbital and the d_π fragment orbital. The better overlap between the two interacting orbitals increases the π-back-donation and the strength of the Fe–CXY interaction.

Table 3

Mulliken population analysis of the systems under investigation and π^* orbital energy of the distorted ligands

								
Fe	s	6.26	6.41	6.39	6.40	6.38	6.17	6.40
	p	12.64	12.77	12.71	12.83	12.80	12.24	12.63
	d	7.23	7.20	7.18	7.17	7.15	7.62	7.21
Axial ligands		35.61	35.38	35.34	35.34	35.32	35.86	35.50
Equatorial ligands		28.26	27.72	27.68	27.70	27.71	36.11	35.53
CXY			22.52	30.70	30.56	38.64		22.73
π^* energy (au)			0.0055	-0.0099	-0.0137	-0.0187		-0.0089
OVERLAP POPULATIONS			FeC_1 0.18	FeC_1 0.11	FeC_1 0.03	FeC_1 0.09		FeC 0.25
			FeO_1 0.03	FeO 0.03	FeS 0.05	FeS_1 0.12		FeO_1 0.02
			C_1O_1 0.32	C_1O 0.32	C_1S 0.13	C_1S_1 -0.01		CO_1 0.31
			C_1O_2 0.56	C_1S 0.36	C_1O 0.55	C_1S_2 0.38		CO_2 0.52
			FeP 0.17	FeP 0.19	FeP 0.19	FeP 0.19		FeP 0.17
			FeC_2 0.17	FeC_2 0.16	FeC_2 0.15	FeC_2 0.13		FeP_1 0.15
			FeC_3 0.05	FeC_3 0.06	FeC_3 0.06	FeC_3 0.09		FeP_2 0.08

The energy required by the ligand deformation is more than compensated by the increased interaction energy.

In all the compounds studied the carbon atom exerts a type of *trans*-influence stronger than that exerted by the oxygen or sulfur atom, as is indicated by the overlap populations reported in Table 3. Indeed, the Fe–C overlap population *trans* to the carbon atom is 0.05, 0.06, 0.09; the Fe–C overlap population *trans* to the oxygen (sulfur) atom is 0.17, 0.15, 0.13 in the complexes with CO_2, COS, CS_2, respectively. Finally it should be noticed the slightly negative charge (-0.04) on the uncoordinated sulfur atom in the CS_2 compound, which shows its nucleophilic character, as is confirmed by the fact that it undergoes alkylation with a variety of electrophiles [13].

Coordination bonding mode of the carbonyl sulphide

The two possible side-on coordination modes of COS, η^2-C,O and η^2-C,S, were analysed and the binding energies, reported in Table 2, are calculated to be -30.9 and -35.8 kcal mol^{-1} with basis I and -26.9 and -44.7 kcal mol^{-1} with basis II, for η^2-C,O and η^2-C,S coordination, respectively. Our analysis thus suggests that COS prefers the η^2-C,S coordination, in agreement with the experimental evidence that no η^2-C,O coordinated carbonyl sulphide complexes have so far been isolated. The main bonding interaction, as deduced from the orbital analysis, is the π-back-donation from the metal to the unsaturated ligand and the strength of this interaction increases as the overlap between the Fe-d_π and the COS-$\pi^\star$ orbitals increases. Indeed, the $\pi^\star$ orbital energies of carbonyl sulphide calculated at the distorted geometries of the complexes are -0.0099 au for η^2-C,O coordination and -0.0137 au for η^2-C,S coordination (see Table 3), indicating a stronger π-back-donation in the latter coordination mode. On the other hand, Table 3 shows that in the basis II calculation the Mulliken population on COS is calculated to be slightly smaller for η^2-C,S coordination (30.56) than for η^2-C,O coordination (30.70), while the opposite is true for the basis I calculation (30.85 for η^2-C,S and 30.81 for η^2-C,O). This could be attributed to the fact that some contribution to the interaction between the iron fragment and the unsaturated ligand also arises from the ligand-to-metal σ-donation and this tends to decrease the total population on the ligand, while the π-back-donation tends to increase it. Since the σ-donation must mainly involve the iron $4s$,$4p$ shell [11], which is poorly described by basis I, the results obtained with this basis set are expected to underestimate the σ-donation. The results of the basis II calculation thus seem to suggest that the σ-donative interaction, as well as the π-back-donation, is also stronger in η^2-C,S coordination mode.

The interaction energy of the compound $Fe(CO)_2(PH_3)_2(\eta^2\text{-COS})$ (η^2-C,O bonded) is lower when basis II is used because of the competition towards π-back-donation between η^2-C,O bonded COS and CO, while that of the η^2-C,S compound is increased because of the better description of the transition metal orbitals, as noted in the previous section. Finally the high, albeit overestimated, interaction energy of $Fe(CO)_2(PH_3)_2(\eta^2\text{-COS})$ (η^2-C,S bonded) suggests that the non-existence of the carbonyl sulphide analogue of $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$ must be ascribed not to a relative instability of the Fe–COS coordination bond but to the presence of competitive reactions, such as carbonylation processes or abstraction of sulfur [1a].

Ligand influence on the Fe–CO_2 moiety

The binding energies of the compound Fe$(PH_3)_4(\eta^2\text{-}CO_2)$ are calculated to be -63.6 and -61.2 kcal mol^{-1} with basis I and basis II, respectively, as shown in Table 2. Analysis of the molecular orbitals shows that the main bonding interaction is the π-back-donation from the transition metal to the unsaturated ligand, as confirmed by the Mulliken analysis data shown in Table 3, which show a population of 22.73 on the carbon dioxide molecule. It is of interest that the Fe–CO_2 interaction causes a decrease of the iron-3*d* population, mainly due to the π-back-donative process.

A comparison between the fragmentation energies of Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and Fe$(PH_3)_4(\eta^2\text{-}CO_2)$ shows that the replacement of carbonyls by phosphines involves a strong increase in the binding energy, which can be accounted for in terms of increased π-back-donation in the tetrakis(phosphine) compound. The fragment orbital Fe-d_π lies at -0.2657 au in Fe$(CO)_2(PH_3)_2$ and at -0.1647 au in Fe$(PH_3)_4$, while the CO_2-$\pi^\star$ orbital energy is 0.0055 au in free CO_2 at the distorted geometry of the complex Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and -0.0089 au for CO_2 with the same geometry as in the complex Fe$(PH_3)_4(\eta^2\text{-}CO_2)$. Thus the replacement of carbonyls by phosphines involves an increase in the overlap between the two interacting orbitals, and the deformation of the CO_2 geometry enhances this effect. The Mulliken analysis results are in agreement with the increased π-back-donation in the tetrakis(phosphine) compound, showing a population of 22.52 for CO_2 in Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and 22.73 for CO_2 in Fe$(PH_3)_4(\eta^2\text{-}CO_2)$.

It is interesting to compare the distorted geometry of the carbon dioxide in the two complexes under analysis. In the tetrakis(phosphine) compound the geometry of the CO_2 is much more distorted, as is shown from the values in Table 1; the deformation energy required for this distortion, however, is more than compensated by the increased interaction energy. Finally the values of the Fe–C and Fe–O bond lengths in the two complexes suggest that the Fe–C bond is stronger than that between iron and oxygen, and this is confirmed by the overlap populations, which are 0.18 and 0.03 for Fe–C and Fe–O in Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ and 0.25 and 0.02 for Fe–C and Fe–O in Fe$(PH_3)_4(\eta^2\text{-}CO_2)$.

Conclusions

A study at "ab initio" LCAO-MO-SCF level of the systems Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, Fe$(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, and Fe$(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ has shown that the main bonding interaction between the fragment Fe$(CO)_2(PH_3)_2$ and the unsaturated molecule CXY is the π-back-donation from the transition metal to the π-acceptor ligand and that the strength of this coordination bond increases in the order $CO_2 < COS < CS_2$, in agreement with the $\pi^\star$ orbital energies of the distorted ligands. Moreover, the π-back-donation is the driving force for the ligand deformation, which allows a better overlap between the $\pi^\star$ ligand and the d_π iron orbitals and so leads to an increased interaction energy.

The η^2-C,S coordination mode of the carbonyl sulphide is preferred over the η^2-C,O mode because of the increased π-back-donation, in keeping with the fact that no η^2-C,O carbonyl sulphide-transition metal complexes have been so far isolated.

The study of the complex Fe$(PH_3)_4(\eta^2\text{-}CO_2)$, a model system for the known compound Fe$(PMe_3)_4(CO_2)$ [3], has shown that the presence of donor ligands such as phosphine, by increasing the electron population at the metal centre, enhances the π-back-donation and hence the strength of the interaction.

Acknowledgment

Thanks are due to the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome) for provision of computing facilities and visiting grants. Support by the Italian National Research Council (CNR), the Ministry of Public Education (MPI), and the U.S. Navy (Grant N00014-86-K-0380) is gratefully acknowledged.

References

1 (a) J.A. Ibers, Chem. Soc. Rev., 11 (1982) 57; (b) D.J. Darensbourg and R.A. Kudaroski, Adv. Organomet. Chem., 22 (1983) 129; (c) T. Ito and A. Yamamoto, in S. Inoue and N. Yamazaki (Ed.), Organic and Bio-organic Chemistry of Carbon Dioxide, Hallsted Press, New York, 1982, chapter 3; (d) R. Eisenberg and D.E. Hendriksen, Adv. Catal., 28 (1979) 119.

2 (a) S. Gambarotta, F. Arena, C. Floriani and P.F. Zanazzi, J. Am. Chem. Soc., 104 (1982) 5082; (b) G. Fachinetti, C. Floriani and P.F. Zanazzi, J. Am. Chem. Soc., 100 (1978) 7405.

3 H.H. Karsch, Inorg. Synth., 20 (1980) 69.

4 (a) M. Aresta, C.F. Nobile, V.G. Albano, E. Forni and M. Manassero, J. Chem. Soc. Chem. Commun., (1975) 636; (b) M. Aresta and C.F. Nobile, J. Chem. Soc. Dalton Trans., (1977) 708.

5 S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, J. Am. Chem. Soc., 107 (1985) 2985.

6 R. Alvarez, E. Carmona, E. Gutierrez-Puebla, J.M. Marín, A. Monge and M.L. Poveda, J. Chem. Soc. Chem. Commun., (1984) 1326.

7 G.S. Bristow, P.B. Hitchcock and M.F. Lappert, J. Chem. Soc. Chem. Commun., (1981) 1145.

8 J.C. Calabrese, T. Herskovitz and J.B. Kinney, J. Am. Chem. Soc., 105 (1983) 5914.

9 H. Werner, Coord. Chem. Rev., 43 (1982) 165.

10 S. Sakaki, K. Kitaura and K. Morokuma, Inorg. Chem., 21 (1982) 760.

11 C. Mealli, R. Hoffmann and A. Stockis, Inorg. Chem., 23 (1984) 56.

12 (a) M.J.S. Dewar, Bull. Soc. Chim. Fr., 18c (1951) 71; (b) J. Chatt and J.A. Duncanson, J. Chem. Soc., (1953) 2939.

13 (a) H. Le Bozec, P.H. Dixneuf, A.J. Carty and N.J. Taylor, Inorg. Chem., 17 (1978) 2568; (b) H. Le Bozec, P.H. Dixneuf, N.J. Taylor and A.J. Carty, J. Organomet. Chem., 135 (1977) C29.

14 H. Tatewaki, Y. Sakai and S. Huzinaga, J. Comput. Chem., 2 (1981) 278.

15 H. Tatewaki and S. Huzinaga, J. Comput. Chem., 1 (1980) 205.

16 Y. Sakai, H. Tatewaki and S. Huzinaga, J. Comput. Chem., 2 (1981) 100.

17 F.B. Van Duijneveldt, IBM J. Res. Dev., (1971) 945.

18 T.H. Dunning Jr., J. Chem. Phys., 53 (1970) 2823.

19 T.H. Dunning Jr. and P.J. Hay, in H.F. Schaefer III (Ed.), Modern Theoretical Chemistry, Plenum, New York, 1977, Vol. 4, p. 1.

20 R. Roos, A. Veillard and G. Vinot, Theor. Chim. Acta, 20 (1971) 1.

21 D.M. Hood, R.M. Pitzer and H.F. Schaefer III, J. Chem. Phys., 71 (1979) 705.

22 A.K. Rappe, T.A. Smedley and W.A. Goddard III, J. Phys. Chem., 85 (1981) 2607.

23 M. Rosi, A. Sgamellotti, F. Tarantelli, C. Floriani and M.F. Guest, J. Chem. Soc. Dalton Trans., in press.

24 S.F. Boys and F. Bernardi, Molec. Phys., 19 (1970) 553.

25 (a) M. Dupuis, D. Spangler and J. Wendolowski, NRCC Software Catalog, Vol. 1, Prog. N. QG01 (GAMESS), 1980; (b) M.F. Guest and J. Kendrick, GAMESS User Manual, Daresbury Technical Memorandum, 1985.

26 S. Gambarotta, M. Pasquali, C. Floriani, A. Chiesi-Villa and C. Guastini, Inorg. Chem., 20 (1981) 1173.

27 (a) T. Herskovitz, J. Am. Chem. Soc., 99 (1977) 2391; (b) R.L. Harlow, J.B. Kinney and T. Herskovitz, J. Chem. Soc. Chem. Commun., (1980) 813.

28 G. Herzberg, Electronic Spectra and Electronic Structure of Polyatomic Molecules, Van Nostrand, Princeton, 1966.

29 R.O. Jones, J. Chem. Phys., 79 (1983) 1885.