7 and/or eq 4 and 5. In principle, the magnitudes of both k_d' and k_r may be solvent-dependent, but it is clear that the k_r step must be quite rapid if it is to compete with relaxation of a higher energy excited state. This is feasible since the k_r represents the rate constant of an outer-sphere electron-transfer reaction involving a very potent reducing agent.

Although only three data points have been measured, the partial action spectrum depicted in Figure 3 suggests that a more complex reaction scheme may actually be required. Since the data were collected under conditions in which the CT state is nearly saturated, the points might be expected to track the excited-state absorption spectrum;[22] however, the data do not follow the published excited-state absorption spectrum (Figure 3).[23] This may indicate that there is more than one reactive excited state or that the efficiency with which the reactive state is populated depends upon the exciting wavelength. Clearly more work will be needed before the dynamics can be understood in detail.

In conclusion, we may note that multiphoton photochemistry may be a common complication associated with photophysical studies using high power lasers. Possibly related biphotonic reactions have previously been reported for $[Ru(bpy)_3]^{2+}$,[24] $[Pt_2(POP)_4]^{4-}$,[25] and $[Cr(bpy)_3]^{3+}$.[26] Since the completion of this work an excited state resonance Raman spectrum of $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline) in methanol has been described.[27]

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Registry No. $[Cu(dmp)_2]^+$, 21710-12-3; $[Cu(dmp)_2]^{2+}$, 14875-91-3; Cl^-, 16887-00-6; CH_2Cl_2, 75-09-2; CH_3CN, 75-05-8; CH_3OH, 67-56-1.

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Interaction between Iron(0) and Heterocumulenes: "Ab Initio" Calculations on the Model Compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$, with X = O, S, NH, CH_2

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"Ab initio" calculations have been performed on the model systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$, with X = O, S, NH, CH_2, to investigate the nature and the energetics of the interaction between iron and heterocumulenes. The results indicate 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 the strength of this coordination bond is found to increase on going from OCX to SCX. In carbonyl sulfide compounds, the stronger back-donative interaction arising in η^2-C,S coordination favors this binding mode over η^2-C,O coordination, and this has been confirmed by partial geometry optimization gradient calculations. Both the weaker π back-donation and the higher deformation energy of CO_2 upon coordination are found to be equally important factors in explaining the low tendency of carbon dioxide, compared to that of CS_2, to bind to transition-metal substrates. The delocalization of electron density on the heterogroup X increases on going from X = CH_2 to X = S in the two studied series of compounds. This trend is found to be strictly related to the different reactivities of the coordinated heterocumulene ligands.

Introduction

The activation of heterocumulenes promoted by transition-metal complexes is a problem of particular interest in organometallic chemistry since heterocumulenes imitate CO_2 in many respects and, therefore, their activation should provide useful information on the problem of CO_2 fixation, which despite intense research activity is not yet completely understood.[1-5] In this context, many interesting studies, which present the synthesis of several transition-metal complexes with heterocumulenes, such as phenyl isothiocyanate and diphenylketene, have recently been reported.[6-16]

Theoretical investigations are limited, at present, to some studies of the interaction between a transition metal and carbon dioxide, carbonyl sulfide, and carbon disulfide.[17-20] These works have clarified that the type of interaction between the transition metal and the unsaturated molecule lies at the very extreme of the Chatt-Dewar-Duncanson model,[21] being dominated by the back-donation from the metal to the heterocumulene. The π back-donation represents the main contribution to the binding energy, and the distortion of the unsaturated ligand upon coordination enhances the stabilization by increasing this interaction.

In this paper we present a theoretical study of the interaction of a transition metal with CO_2 and a series of molecules struc-

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turally related to it, such as carbonyl sulfide, carbon disulfide, ketene, thioketene, hydrogen isocyanate, and hydrogen isothiocyanate. We have used the model metallic fragment $Fe(CO)_2(PH_3)_2$ as a binding substrate for the cumulene molecules. This choice is justified by the existence of the well-characterized related complex $Fe(CO)_2(PMe_3)(PPh_3)(\eta^2\text{-}CS_2)$.[22]

The systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$, with X = O, S, CH_2, NH, have been investigated with "ab initio" Hartree–Fock MO calculations, and all the geometrical parameters involved in the bond between the iron and the unsaturated ligand have been optimized by means of gradient calculations.

The aim of the present work is to investigate the nature and the energetics of the interaction between the iron and the unsaturated ligand and to elucidate how the nature of the heterocumulene (i.e. of the heteroatom) affects the strength of the interaction.

Computational Details

Basis Sets. Two Gaussian basis sets, hereafter denoted as I and II, have been employed throughout this work. In basis I, the functions for iron were derived from Huzinaga's MINI-4 basis,[23] by splitting the outermost s and d functions. The MINI-1 basis[24,25] was used for the phosphorus atoms and the carbonyl groups, and a (2s) contraction[24] of Van Duijneveldt's (4s) primitive set[26] was adopted for the phosphine hydrogens. For the component atoms of the unsaturated ligand, i.e. CO_2, COS, OCNH, $OCCH_2$, CS_2, SCNH, and $SCCH_2$, Dunning's basis set[27,28] of double-ζ quality was employed. All geometrical optimizations described herein were carried out by using this basis. Subsequent single-point SCF calculations at the optimized geometries were performed by using the more extended basis II. Here the s,p basis for iron was taken from the (12s6p4d) set of ref 29, with the addition of two basis functions to describe the 4p orbital,[30] while the Fe d basis was the reoptimized (5d) set of ref 31, contracted (4/1). This leads to an (11s8p5d) primitive basis for iron, contracted (8s6p2d). The same double-ζ set[27,28] employed in basis I to describe the heterocumulene molecules was used in basis II for all the ligand atoms.

The reliability of such basis sets has been checked in a previous study on the interaction of iron and formaldehyde.[32] In particular, the basis set superposition error has been evaluated according to Boys and Bernardi[33] and found to be acceptably small (3.9 kcal·mol^{-1} with basis I, 4.6 kcal·mol^{-1} with basis II).

"Ab initio" spin-restricted Hartree–Fock SCF gradient calculations were used in partial geometry optimizations of the complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCNH)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCNH)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$ and in deriving estimates of the binding energies of all the complexes with respect to free OCX or SCX (with X = O, S, NH, CH_2) and the iron-fragment species. Dissociation to these fragments may lead to either singlet or triplet products. In a previous study[32] configuration interaction calculations on the complex $Fe(CO)_4(\eta^2\text{-}CH_2O)$ allowed 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} in free formaldehyde.[34] A $S_0 \rightarrow T_1$ value of 74.7 kcal·mol^{-1} is present in free carbon disulfide,[34] and the lowest lying triplet in free carbon dioxide is 113 kcal·mol^{-1} above the singlet ground state.[35] Comparable singlet–triplet separations should be present in carbonyl sulfide,[34] ketene,[34] thioketene,[36] hydrogen isocyanate,[37] and hydrogen isothiocyanate.[38] Therefore, it is reasonable to assume with some confidence that fragmentation of the complexes under examination should lead to singlet products, even 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.[22b]

All computations were performed by using the GAMESS program package,[39] implemented on the cluster of FPS-164 processors at the IBM European Center for Scientific and Engineering Computing (ECSEC, Rome, Italy).

Geometries and Geometry Optimization. In all the calculations described herein we have confined our attention to geometries involving side-on coordination of the OCX and SCX ligands, since experimental evidence[1-5] and theoretical considerations[17,18] suggest that this coordination mode should be preferred.

For metallic fragments such as $Fe(CO)_2(PH_3)_2$, having two potential coordination sites available, only the side-on coordination for CO_2 and CS_2 should be attainable. Indeed, the η^2-C,S coordination mode is the only one characterized by X-ray crystallography or IR and NMR spectra for monometallic complexes with CS_2[1,3,22,40,41] as well as for the very few examples of transition-metal compounds containing COS.[42-44] However, we have considered also the η^2-C,O coordination of COS to analyze the effect of the substitution of the uncoordinated oxygen atom of CO_2.

In the compounds of $Fe(CO)_2(PH_3)_2$ with hydrogen isocyanate, hydrogen isothiocyanate, ketene, and thioketene, the side-on coordination mode should still be preferred with respect to end-on or C-coordination but the site of attack can be different from that of the C=O or C=S bond. The η^2-C,O coordination is preferred for ketene by early transition metals, such as titanium[11] and vanadium,[10] while metals such as manganese and platinum prefer to attack the C=C bond.[15,16] Experimental evidence suggests that the hydrogen isocyanate molecule prefers the η^2-C,N coordination,[9,45] while hydrogen isothiocyanate, as well as thioketene, prefers the η^2-C,S coordination.[3,6-8]

We have performed an "ab initio" MO study[46] on the coordination bonding mode of hydrogen isocyanate and hydrogen isothiocyanate toward the $Fe(CO)_2(PH_3)_2$ fragment, and we have found that the η^2-C,N coordination is slightly preferred relative to the η^2-C,O mode by hydrogen isocyanate (by 3.9 kcal·mol^{-1}), while hydrogen isothiocyanate prefers the η^2-C,S coordination, with respect to the η^2-C,N mode, by 10.3 kcal·mol^{-1}.

In conclusion, the η^2-C,S coordination should be preferred in the SCX compounds, while the η^2-C,O coordination seems not attainable for the complexes of $Fe(CO)_2(PH_3)_2$ with COS, OCNH, and $OCCH_2$. Nevertheless, we have focused our attention on the η^2-C,O coordination since the goal of our work is to understand the nature of the Fe–CO_2 coordination bond and to analyze the effects of the substitution of the heteroatom, in order to get useful information on the fixation of CO_2.

In the partial geometry optimization calculations we have optimized the geometrical parameters involving the iron atom and the atoms of the unsaturated ligand OCX or SCX, except for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, where the bond angles and distances relative to the interaction Fe–CS_2 were derived directly from the experimental structure of $Fe(CO)_2$-

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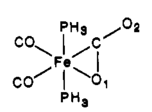
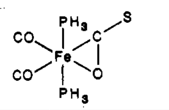
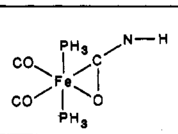
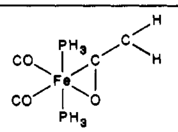
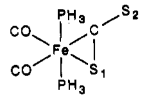
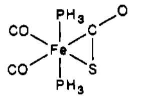
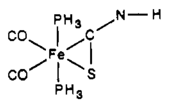
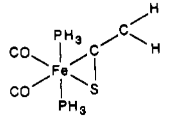
Table I. Partially Optimized Geometries of the Systems under Investigation[a]

							
Fe-C	1.842	Fe-C	1.852	Fe-C	1.821	Fe-C	1.862
Fe-O$_1$	2.124	Fe-O	2.101	Fe-O	2.114	Fe-O	2.029
C-O$_1$	1.247	C-O	1.230	C-O	1.268	C-O	1.275
C-O$_2$	1.217	C-S	1.689	C-N	1.273	C-C	1.337
∠O$_1$-C-O$_2$	140.5	∠O-C-S	139.0	∠O-C-N	141.6	∠O-C-C	138.8
∠C-Fe-CO	96.0	∠C-Fe-CO	96.9	∠C-Fe-CO	94.0	∠C-Fe-CO	96.9
				∠H-N-C	115.5	∠H-C-C	121.1
				N-H	1.010	C-H	1.074

							
Fe-C	1.983	Fe-C	1.857	Fe-C	1.855	Fe-C	1.893
Fe-S$_1$	2.335	Fe-S	2.457	Fe-S	2.466	Fe-S	2.415
C-S$_1$	1.676	C-S	1.767	C-S	1.778	C-S	1.763
C-S$_2$	1.615	C-O	1.202	C-N	1.261	C-C	1.330
∠S$_1$-C-S$_2$	138.9	∠S-C-O	138.0	∠S-C-N	139.1	∠S-C-C	134.9
∠C-Fe-CO	92.3	∠C-Fe-CO	94.3	∠C-Fe-CO	91.5	∠C-Fe-CO	88.5
				∠H-N-C	117.6	∠H-C-C	122.2
				N-H	1.009	C-H	1.077

[a] Bond lengths are in angstroms and angles in degrees. The Fe(CO)$_2$(PH$_3$)$_2$(η^2-CS$_2$) geometry has been deduced from the experimental structure of Fe(CO)$_2$(PMe$_3$)(PPh$_3$)(η^2-CS$_2$) (see text).

(PMe$_3$)(PPh$_3$)(η^2-CS$_2$).[22b] The geometry of the Fe(CO)$_2$(PH$_3$)$_2$ group has been taken from ref 32 and kept frozen during the optimizations. No geometry optimization has been performed for the dissociated species: the geometry of the Fe(CO)$_2$(PH$_3$)$_2$ fragment has been taken equal to that in the complexes, while the experimental geometries have been used for CO$_2$,[34] COS,[34] CS$_2$,[34] OCNH,[47] SCNH,[48] OCCH$_2$,[49] and SCCH$_2$.[36]

The optimized structures of the complexes under investigation are shown in Table I. All the compounds can be viewed as either a distorted trigonal bipyramid with a five-coordinated iron atom, or a distorted octahedron, with a six-coordinated iron atom, depending on whether one considers the unsaturated ligand OCX (or SCX) to be monodentate or bidentate. The iron atom is bonded to two mutually trans phosphines in the axial sites and to two carbonyls and OCX (or SCX) in the equatorial sites.

The partially optimized structures of Table I show that the Fe–C bond length is shorter than the Fe–O one in all the systems with OCX, and this trend is in agreement with the experimental structure of the known carbon dioxide–transition-metal complexes, where the CO$_2$ is η^2-bonded to the metal. The M–C and M–O bond lengths are respectively 1.84 and 1.99 Å in [Ni(PCy$_3$)$_2$(η^2-CO$_2$)]·0.75C$_7$H$_8$,[50] 2.112 and 2.160 Å in [(C$_5$H$_5$)$_2$Mo(η^2-CO$_2$)],[51] 2.144 and 2.173 Å in [Nb(η-C$_5$H$_4$Me)$_2$(CH$_2$SiMe$_3$)(η^2-CO$_2$)],[52] and 2.105 and 2.147 Å in [Mo(PMe$_3$)$_3$(CN-*i*-Pr)(η^2-CO$_2$)$_2$].[53] The computed C–O bond lengths vary between 1.230 and 1.275 Å, and these values are comparable with those observed in the complexes with CO$_2$, which lie between 1.22 and 1.29 Å.[50-53] The smallest value, 1.230 Å, is calculated for the compound with COS, where the C–O double bond is essentially retained. The angles ∠O–C–X are computed to be 138.8, 139.0, 140.5, and 141.6° for X = CH$_2$, S, O, and NH, respectively, and these values are slightly larger than the ∠O–C–O experimental ones, which are around 133°,[50-53] but they are very close to the theoretically optimized value for the model system Ni(PH$_3$)$_2$(η^2-CO$_2$), which is 139°.[17]

In the compounds with SCX, the C–S bond lengths vary between 1.676 and 1.778 Å: these values are always longer than those exhibited by the free ligands (CS$_2$, 1.55 Å;[34] COS, 1.56 Å;[34] SCNH, 1.57 Å;[48] SCCH$_2$, 1.55 Å[36]), but they are shorter than typical C–S single bonds (1.80–1.82 Å).[54] Finally, we can notice that the optimized geometry of the compound with OCCH$_2$ is in reasonable agreement with the experimental structure of Cp$_2$V(η^2-OCCPh$_2$) (C–O, 1.29 Å; C–C, 1.34 Å; ∠O–C–C, 135.9°)[10] and the optimized structure of Fe(CO)$_2$(PH$_3$)$_2$(η^2-SCNH) is in line with the experimental one of (C$_5$H$_5$)$_2$V(η^2-SCNPh) (C–S, 1.745 Å; C–N, 1.265 Å; ∠S–C–N, 138.6°).[6]

Results and Discussion

The total SCF energies of the complexes investigated and of their relative free fragments are reported in Table II, together with the estimated binding energies. The binding energies have been computed as the difference between the energy of the complexes and the energy of the separated fragments. Since in computing these energies we have used partially optimized geometries for the complexes and nonoptimized geometries for the free iron fragment, we expect our data to overestimate somewhat (in absolute value) the true fragmentation energies of the complexes. However, this should not affect the main qualitative conclusions of our comparative analysis.

In our model the binding energy (BE) can be thought of as the sum of a positive deformation energy (DEF) arising from the distortion of the unsaturated ligand and a negative interaction energy (INT) resulting from the interaction between the iron fragment and the distorted ligand.[17] The deformation and interaction energies are also reported in Table II.

Study of the Interaction between Fe(CO)$_2$(PH$_3$)$_2$ and OCX (with X = O, S, NH, CH$_2$). As can be seen from Table II, the strength of the coordination bond for these complexes goes in the order OCCH$_2$ > COS > OCNH > CO$_2$, for the η^2-C,O coordination. However, it is interesting to note the very different roles played by the deformation and interaction contributions in the determination of the overall binding energies of the various complexes. For instance, although the binding energy of Fe(CO)$_2$(PH$_3$)$_2$(η^2-OCCH$_2$) is computed to be substantially larger than that of the other three complexes, its interaction energy is comparable to that of the OCNH compound, whose net binding energy is substantially lowered by the relatively high energy required for OCNH deformation. In contrast, COS exhibits a small interaction

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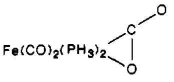
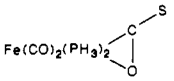
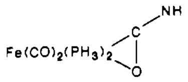
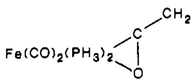
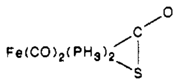
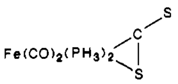
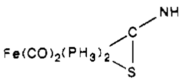
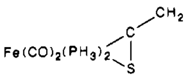
Table II. Total SCF Energies (hartree) and Interaction (INT), Deformation (DEF), and Binding (BE) Energies (kcal·mol^{-1}) of the Analyzed Systems (See Text)

complex	SCF energies basis I	SCF energies basis II		binding energies basis I	binding energies basis II
	-2350.4204	-2359.6477	INT	-63.5	-56.8
			DEF	37.3	37.3
			BE	-26.2	-19.5
	-2673.0489	-2682.2803	INT	-62.5	-58.5
			DEF	31.6	31.6
			BE	-30.9	-26.9
	-2330.5634	-2339.7929	INT	-75.6	-70.4
			DEF	46.9	46.9
			BE	-28.7	-23.4
	-2314.5575	-2323.7919	INT	-72.4	-70.2
			DEF	34.9	34.9
			BE	-37.7	-35.5
	-2673.0567	-2682.3087	INT	-67.7	-76.6
			DEF	31.9	31.9
			BE	-35.8	-44.7
	-2995.6767	-3004.9334	INT	-66.2	-78.0
			DEF	27.1	27.1
			BE	-39.1	-50.9
	-2653.2113	-2662.4622	INT	-83.5	-91.7
			DEF	40.6	40.6
			BE	-42.9	-51.1
	-2637.2102	-2646.4597	INT	-90.8	-98.1
			DEF	32.4	32.4
			BE	-58.4	-65.7

fragment	SCF energies basis I	SCF energies basis II	fragment	SCF energies basis I	SCF energies basis II
$Fe(CO)_2(PH_3)_2$	-2162.8254	-2172.0633	$OCCH_2$	-151.6720	-151.6720
CO_2	-187.5533	-187.5533	CS_2	-832.7890	-832.7890
COS	-510.1742	-510.1742	SCNH	-490.3175	-490.3175
OCNH	-167.6923	-167.6923	$SCCH_2$	-474.2917	-474.2917

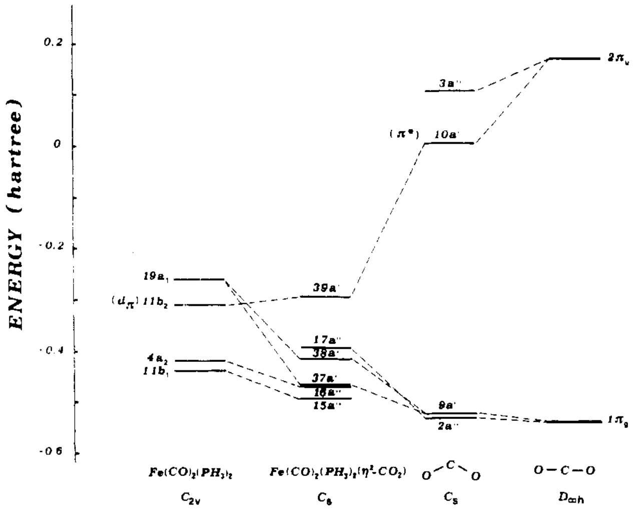


Figure 1. Molecular orbital correlation diagram of $Fe(CO)_2(PH_3)_2$-(η^2-CO_2).

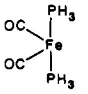
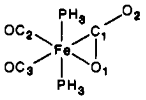
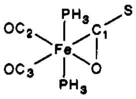
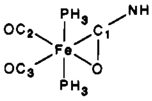
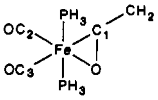
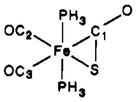
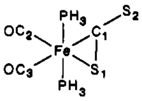
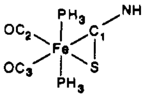
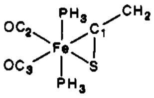
energy, comparable to that of CO_2, and a strong coordination bond due to the low COS deformation energy. The coordination bond between the iron and the carbon dioxide is computed to be the weakest one because of the lower interaction energy of CO_2, compared to those of OCNH and $OCCH_2$, and the higher deformation energy of CO_2, compared to that of COS. As a general conclusion based on our calculations of the interaction between a strongly Lewis-basic metal site and the organic functionality >C=X, it seems that a major factor determining the binding energy is the deformation energy of the cumulene structure.

All the interaction energies decrease upon extension of the basis set on the iron substrate from basis I to basis II, and the largest variation (6.7 kcal·mol^{-1}) is found in the compound with CO_2.

To understand qualitatively the nature of the coordination bond between the iron substrate and the OCX ligand, it is useful to analyze the correlation between the molecular orbitals of the complex and those of the free 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, where only the main correlations are reported. To emphasize the effects of CO_2 distortion upon complex formation, Figure 1 also shows the orbital energy levels of free CO_2 both at its equilibrium geometry and at the C_s geometry of the complex. As we see, the orbitals mainly involved in the iron–carbon dioxide bonding are 37a′, 38a′, and 39a′, while the 17a″ orbital is a nonbonding orbital localized in the CO_2 group. The 37a′ and 38a′ molecular orbitals originate from the interaction of the $Fe(CO)_2(PH_3)_2$ $19a_1$ and CO_2 9a′($1\pi_g$) filled orbitals. This is a four-electron destabilizing interaction. Effective bonding, therefore, is concentrated in the 39a′ orbital, which is the bonding combination of the $Fe(CO)_2(PH_3)_2$ $11b_2$ orbital (hereafter denoted as d_π) and the virtual orbital of CO_2 10a′($2\pi_u$) (hereafter denoted as π^*). The former orbital is mainly iron 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. Figure 1 shows also that the CO_2 distortion upon coordination lowers the π^* orbital energy and reduces the gap between this orbital and the fragment d_π orbital. The distortion of CO_2 implies therefore an increased π back-donation.

The other complexes show the same bonding picture: the main bonding orbital in all the compounds can be seen as the overlap between the $Fe(CO)_2(PH_3)_2$ d_π and the ligand π^* orbitals. The main bonding interaction in all the systems under investigation is thus the π back-donation from the transition metal to the unsaturated molecule as is confirmed also by the Mulliken population analysis, reported in Table III, which assigns a net negative charge to the heterocumulene molecules.

Table III. Mulliken Population Analysis (e) of the Systems under Investigation and π* Orbital Energy (au) of the Deformed Ligands

		orbital population		π* energy	overlap population (basis II)	
		basis I	basis II			
	Fe s	5.94	6.26			
	p	11.99	12.64			
	d	7.47	7.23			
	ax ligands	36.00	35.61			
	eq ligands	28.60	28.26			
	Fe s	5.87	6.41	0.0055	FeC_1	0.18
	p	12.01	12.77		FeO_1	0.03
	d	7.26	7.20		C_1O_1	0.32
	ax ligands	35.88	35.38		C_1O_2	0.56
	eq ligands	28.24	27.72		FeP	0.17
	$O_1C_1O_2$	22.74	22.52		FeC_2	0.17
					FeC_3	0.05
	Fe s	5.87	6.39	−0.0099	FeC_1	0.11
	p	12.01	12.71		FeO	0.03
	d	7.23	7.18		C_1O	0.32
	ax ligands	35.86	35.34		C_1S	0.36
	eq ligands	28.22	27.68		FeP	0.19
	OC_1S	30.81	30.70		FeC_2	0.16
					FeC_3	0.06
	Fe s	5.88	6.40	0.0069	FeC_1	0.16
	p	12.00	12.74		FeO	0.03
	d	7.23	7.19		C_1O	0.36
	ax ligands	35.88	35.38		C_1N	0.61
	eq ligands	28.22	27.71		FeP	0.17
	OC_1NH	22.79	22.58		FeC_2	0.16
					FeC_3	0.05
					NH	0.30
	Fe s	5.86	6.40	0.0281	FeC_1	0.19
	p	12.01	12.73		FeO	0.05
	d	7.20	7.19		C_1O	0.37
	ax ligands	35.88	35.39		C_1C	0.53
	eq ligands	28.26	27.78		FeP	0.16
	OC_1CH_2	22.79	22.51		FeC_2	0.15
					FeC_3	0.07
					CH	0.35
	Fe s	5.89	6.40	−0.0137	FeC_1	0.03
	p	12.00	12.83		FeS	0.05
	d	7.21	7.17		C_1S	0.13
	ax ligands	35.84	35.34		C_1O	0.55
	eq ligands	28.21	27.70		FeP	0.19
	SC_1O	30.85	30.56		FeC_2	0.15
					FeC_3	0.06
	Fe s	5.88	6.38	−0.0187	FeC_1	0.09
	p	12.01	12.80		FeS_1	0.12
	d	7.15	7.15		C_1S_1	−0.01
	ax ligands	35.84	35.32		C_1S_2	0.38
	eq ligands	28.18	27.71		FeP	0.19
	$S_1C_1S_2$	38.94	38.64		FeC_2	0.13
					FeC_3	0.09
	Fe s	5.89	6.38	−0.0167	FeC_1	0.04
	p	12.01	12.78		FeS	0.05
	d	7.16	7.15		C_1S	0.14
	ax ligands	35.84	35.33		C_1N	0.61
	eq ligands	28.19	27.70		FeP	0.18
	SC_1NH	30.91	30.66		FeC_2	0.15
					FeC_3	0.07
					NH	0.31
	Fe s	5.89	6.38	−0.0120	FeC_1	0.14
	p	12.00	12.78		FeS	0.12
	d	7.13	7.16		C_1S	0.08
	ax ligands	35.83	35.34		C_1C	0.50
	eq ligands	28.23	27.76		FeP	0.17
	SC_1CH_2	30.92	30.58		FeC_2	0.12
					FeC_3	0.07
					CH	0.39

The results of Table III show that the coordination of OCX implies a flow of electron density from the ligands CO and PH_3 toward the iron and then to the unsaturated molecule. We note, however, that the net negative charge on OCX is computed to be appreciably smaller (by 0.11 e for COS, 0.21 e for OCNH, 0.22 e for CO_2, and 0.28 e for $OCCH_2$) when using basis II than when using basis I. This suggests the presence of a small ligand-to-metal σ-donative contribution to the interaction between iron and OCX, which is better described by basis II than by basis I. Indeed, it seems clear that the σ-donative interaction should strongly involve the empty iron 4p orbital,[18] which is satisfactorily described by basis II but not by basis I. As can be seen from Table

Table IV. Energies (hartree) and Mulliken Populations (%) of the Bonding Orbital between the Iron Fragment and the Heterocumulene Ligand in the Analyzed Systems

	ligand							
	CO_2	COS[a]	OCNH	$OCCH_2$	COS[b]	CS_2	SCNH	$SCCH_2$
orbital	39a′	42a′	39a′	39a′	42a′	45a′	42a′	42a′
energy	−0.2951	−0.2616	−0.3032	−0.3060	−0.2875	−0.2581	−0.2895	−0.2935
Fe	36	17	34	38	29	17	26	27
C	13	6	14	18	12	9	13	10
X	13[c]	4[c]	18[c]	25[c]	28[d]	11[d]	33[d]	52[d]
Y	27[e]	69[f]	24[g]	8[h]	23[e]	59[f]	21[g]	3[h]

[a] η^2-C,O-bonded. [b] η^2-C,S-bonded. [c] X = O. [d] X = S. [e] Y = O. [f] Y = S. [g] Y = NH. [h] Y = CH_2.

III, the iron p-orbital populations are almost identical in the fragment and in the complexes when basis I is used, whereas the population is larger in the complexes, and particularly in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, when basis II is used. We notice that a better described σ interaction does not correspond, in the basis II calculation, to an increase in the interaction energies. It should be considered, however, that the larger basis set improves substantially the description of both the σ and π interactions between the metal fragment and the carbonyl and phosphine ligands, implying an overall stronger competition toward coordination between these ligands and the η^2-C,O-bonded heterocumulene molecules.

The strength of the π back-donation can be related to the π^*-orbital energy of the OCX ligand. A lower π^* energy implies a smaller energy gap between this orbital and the filled d_π iron orbital, and this enhances the strength of the back-donative interaction. The distortion of the OCX ligands upon coordination can also be viewed in this context, since the deformation causes an energy lowering of the π^* orbital. The π^* energy is computed to be 0.2167, 0.1723, 0.1162, and 0.1084 au for free (undistorted) OCNH, CO_2, $OCCH_2$, and COS, respectively, and decreases to 0.0069, 0.0055, 0.0281, and −0.0099 au, respectively, upon distortion. These values suggest that the π back-donation increases in the order $OCCH_2 < OCNH \leq CO_2 <$ COS. This trend cannot be directly related with the interaction energy, which increases in the order $CO_2 < COS \ll OCCH_2 \simeq OCNH$. This discrepancy can be understood by considering the electron-density maps of the bonding orbital of the analyzed systems, reported in Figure 2. These maps show that the delocalization of the electron density toward the heterogroup increases in the order $OCCH_2 < OCNH \simeq CO_2 \ll COS$. This trend is confirmed by the Mulliken populations of the bonding orbitals of the complexes under investigation, reported in Table IV, which show a low delocalization (8%) on the CH_2 group in the bonding orbital of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$ and a very high delocalization (69%) on the S atom in the bonding orbital of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$. Therefore, the bond between the iron fragment and the COS molecule is not as strong as one could expect by considering just the π back-donation since there is a high delocalization of the electron density on the sulfur atom, while in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$ there is a strong bond, since almost all the electron density is localized in the Fe–CO moiety.

Therefore, the trend of the interaction energy $CO_2 < COS \ll OCCH_2 \simeq OCNH$ can be explained by taking into account at the same time the strength of the π back-donation and the delocalization of the electron density on the heterogroup. We may also notice that the sulfur atom in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$ has a high nucleophilic character and, therefore, this compound should undergo alkylation very easily. On the other hand, the compound with ketene should present a different reactivity, in agreement with the experimental evidence that $Cp_2V(\eta^2\text{-}OCCPh_2)$ does not react with CH_3I, even under drastic conditions.[10] $[Cp_2Zr(\eta^2\text{-}OCCH_2)CH_3]Na{\cdot}2THF$ reacts with CH_3I, but the NMR spectroscopic and structural data do not indicate a high negative charge density at the CH_2 group.[13]

Study of the Interaction between $Fe(CO)_2(PH_3)_2$ and SCX (with X = O, S, NH, CH_2). The compounds of $Fe(CO)_2(PH_3)_2$ with SCX show a bonding structure entirely comparable to the one described for the analogous compounds with OCX. The molecular orbital analysis again shows that in all the analyzed compounds there is essentially one bonding orbital that describes a π back-donative interaction between the iron d_π orbital and the π^* orbital of the unsaturated ligand.

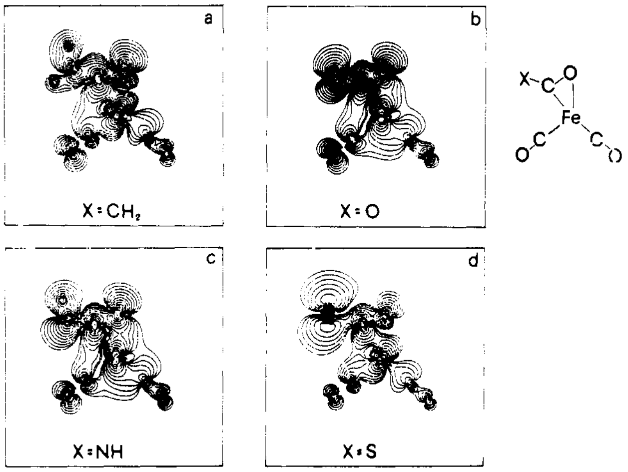


Figure 2. Electron density in the *xy* plane of the bonding orbital between Fe and OCX for (a) $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$, (b) $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$ (c) $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCNH)$, and (d) $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$. Frames are 20 × 20 au. All contours are in $e{\cdot}au^{-3}$ and include 64.7837, 16.1959, 4.0490, 1.0122, 0.5061, 0.2531, 0.1265, 0.0633, 0.0316, 0.0158, 0.0079, 0.0040, 0.0020, and 0.0010.

The Mulliken population analysis, whose results are reported in Table III, confirms this picture since it assigns a net negative charge to the SCX ligands. It is interesting to notice that this charge is computed to be appreciably smaller (by 0.25 e for SCNH, 0.29 e for COS, 0.30 e for CS_2, and 0.34 e for $SCCH_2$) when basis II is used than when basis I is used and the difference is greater than that of the analogous compounds with OCX. This suggests that the ligand-to-metal σ-donative interaction, which involves strongly the empty iron 4p orbital, is more important for these complexes with SCX, compared to the interaction for the complexes with OCX. The π and nonbonding orbital energies of the SCX ligands (not reported in the tables) result to be systematically about 0.1 au higher than those of the corresponding OCX ligands. This fact provides further evidence for the above conclusion. Indeed, as we see from Table II, upon extension of the basis set on the iron substrate from basis I to basis II, the interaction energy for the SCX compounds increases substantially (by about 8–12 kcal·mol^{-1}), confirming the presence of a source of interaction that basis II describes better than basis I. The π back-donative interaction is also stronger in the compounds with SCX, compared to the analogous complexes with OCX, as is suggested by the values of the interaction energy (see Table II) and, particularly, by the π^* orbital energies of the deformed ligands, reported in Table III.

It is interesting to note that the π^* energy of COS, which is −0.0099 au for COS at the distorted geometry of the compound where it is η^2-C,O-bonded, is lowered to −0.0137 au when COS is η^2-C,S-bonded to the iron. Therefore, the η^2-C,S coordination of the carbonyl sulfide is preferred, with respect to the η^2-C,O mode, because of the increased π back-donation, in agreement with the experimental evidence that no η^2-C,O carbonyl sulfide–transition-metal complexes have been isolated so far.

In the analyzed series the π back-donation increases in the order $SCCH_2 < COS < SCNH < CS_2$, while the interaction energy rises in the order $COS < CS_2 \ll SCNH < SCCH_2$. As already noted for the OCX compounds, the trend of the interaction energy cannot be directly related to that of the π back-donation, although this is the main bonding interaction, but it is necessary to take into account also the delocalization of the electron density toward the heterogroup, which increases in the order $SCCH_2 < SCNH \simeq COS \ll CS_2$ (see Table IV). The bond between the iron and the CS_2 molecule is weaker than what one might expect by considering just the π back-donation since there is a high delocalization of the electron density on the S atom (59%), while in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$ we have a strong bond since almost all the electron density is localized in the Fe–CS moiety (only 3% of the electron density is localized in the CH_2 group).

Again we can notice that the high nucleophilic character of the uncoordinated sulfur atom in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$ is confirmed by the experimental evidence that it undergoes alkylation with a variety of electrophiles,[22] while the CH_2 group in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$ should not be attacked by alkylating agents, such as CH_3I.

It is interesting to note also that in all the analyzed systems the carbon atom induces a trans influence stronger than that due to the oxygen (or sulfur) atom, as is suggested by the overlap populations reported in Table III. Indeed, the overlap population of the Fe–C bond trans to the carbon atom is 0.05–0.09 e, while that of the Fe–C bond trans to the oxygen (or sulfur) atom is 0.12–0.17 e. From Table III we can see also that the C–S bond in the SCX series is weaker than the C–O bond in the OCX series: indeed, the C–S overlap population varies between –0.01 e in the compound with CS_2 and 0.14 e in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCNH)$, while the C–O overlap population assumes values between 0.32 and 0.37 e. This is more evidence that the SCX ligand gives rise to a stronger coordination bond than the analogous OCX molecule.

Conclusions

The study at the "ab initio" Hartree–Fock level of the systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCX)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCX)$ (with X = O, S, NH, CH_2) has shown 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 the strength of this coordination bond increases on going from OCX to SCX. Moreover, the π back-donation is the driving force of the ligand deformation, which allows a better overlap between the π^* ligand and the d_π iron orbitals and, therefore, leads to an increased interaction energy.

Our results confirm that the low reactivity of carbon dioxide, compared to that of CS_2, toward transition-metal fragments is mainly due to the weaker π acidity exhibited by this molecule. The preference of the carbonyl sulfide for the η^2-C,S coordination can be explained in the same context: this coordination bonding mode is preferred, with respect to the η^2-C,O mode, because of the increased π back-donation, in agreement with the experimental evidence that no η^2-C,O carbonyl sulfide–transition-metal complexes have been isolated so far.

In the two analyzed series of compounds of $Fe(CO)_2(PH_3)_2$ with OCX and SCX, the delocalization of electron density on the heterogroup increases on going from X = CH_2 to X = S, suggesting that the uncoordinated sulfur atom in the compounds with COS and CS_2 has a high nucleophilic character, while the CH_2 group in the compounds with ketene and thioketene should not undergo alkylation very easily.

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Registry No. $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CO_2)$, 110174-28-2; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}COS)$, 110174-29-3; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCNH)$, 110174-30-6; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}OCCH_2)$, 110174-31-7; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CS_2)$, 110174-32-8; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CSO)$, 110174-34-0; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCNH)$, 110174-33-9; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}SCCH_2)$, 110174-35-1; Fe, 7439-89-6.

Notes

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Reactions of the Dirhenium(III) Carboxylate Complexes $Re_2(O_2CR)_2X_4L_2$ (R = Me, Et; X = Cl, Br; L = H_2O, py, 4-Mepy) with the Monodentate Phosphines PPh_3 and Ph_2Ppy. Complexes of the Paramagnetic Re_2^{5+} Core That Contain a Single Carboxylate Bridge

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While the dirhenium(III) complexes $Re_2(O_2CR)_2X_4$ (X = Cl, Br) and their 1:2 adducts $Re_2(O_2CR)_2X_4L_2$ (L = H_2O, py, 4-Mepy, DMF, Me_2SO, Ph_3PO) have been known for several years and their syntheses, structures, and spectroscopic properties are quite well documented,[1–3] an examination of their chemiccal reactivity has been largely neglected. Recently, we studied the reactions of several complexes of the type $Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; R = Me, Et; L = H_2O, py, DMF, Me_2SO) with monodentate tertiary phosphines in alcohol solvents.[4,5] Whereas $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = H_2O, py) react with PMe_3, PMe_2Ph, and $PMePh_2$ to give the dirhenium(II) complexes $Re_2Cl_4(PR_3)_4$, the novel dirhenium(IV,II) alkoxide complexes $(R'O)_2X_2ReReX_2(PPh_3)_2$ were produced in the reactions between $Re_2(O_2CR)_2X_4L_2$ (X = Cl, Br; R = Me, Et; L = H_2O, DMF, Me_2SO) and PPh_3 in refluxing alcohol solvents R′OH (R′ = Me, Et, *n*-Pr, *i*-Pr).[4,5] During the course of these investigations we noted that the reactions between $Re_2(O_2CCH_3)_2Cl_4L_2$ (L = py, 4-Mepy) and PPh_3 in refluxing ethanol did not yield $(EtO)_2Cl_2ReReCl_2(PPh_3)_2$. Since we did not understand why these reactions should be different, we have now examined them in further detail and discovered that they yield a derivative of the paramagnetic dirhenium(II,III) core viz. $Re_2(O_2CCH_3)Cl_4(PPh_3)_2$. The chemistry of this and related systems is described in the present report.

Experimental Section

Starting Materials. The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br) were synthesized as described in the literature.[6,7] These were converted

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