7 and/or eq 4 and 5. In principle, the magnitudes of both $k_d$ and $k$, may be solvent-dependent, but it is clear that the $k_e$ step must be quite rapid if it is to compete with relaxation of a higher energy excited state. This is feasible since the $k_e$ 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;26 however, the data do not follow the published excited-state absorption spectrum (Figure 3).25 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 $[\text{Ru(bpy)}]^{2+}$,24 $[\text{Pt}^{2+} \text{(POP)}]^{2+}$,22 and $[\text{Cr(bpy)}]^{3+}$,22 Since the completion of this work an excited state resonance Raman spectrum of $[\text{Cu(dpdp)}]^{2+}$ (dpdp = 2,9-diphenyl-1,10-phenanthroline) in methanol has been described.27

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Registry No. $[\text{Cu(dmp)}]^{2+}$, 21710-12-3; $[\text{Cu(dmp)}]^{3+}$, 14875-91-3; $\text{Cl}^{-}$, 16887-00-6; $\text{CH}_2\text{Cl}_2$, 75-09-2; $\text{CH}_3\text{CN}$, 75-05-8; $\text{CH}_3\text{OH}$, 67-56-1.

(22) The analysis assumes that only sequential two-photon absorption occurs and that the second photon is absorbed by the thermally equilibrated CT state. This is probably an oversimplification.


Interaction between Iron(0) and Heterocumulenes: "Ab Initio" Calculations on the Model Compounds Fe(CO)$_2$(PH$_3$)$_2$($\eta^2$-OCX) and Fe(CO)$_2$(PH$_3$)$_2$($\eta^2$-SCX), with X = O, S, NH, CH$_2$

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Received February 20, 1987

"Ab initio" calculations have been performed on the model systems Fe(CO)$_2$(PH$_3$)$_2$($\eta^2$-OCX) and Fe(CO)$_2$(PH$_3$)$_2$($\eta^2$-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 $\pi$-backdonation from the metal to the heterocumulene. The back-donation and the higher deformation energy of CO, back-donation from the metal to the heterocumulene. The delocalization of electron density on the heterogroup X increases on going from O2CO2 to 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.

In this paper we present a theoretical study of the interaction of a transition metal with CO$_2$ and a series of molecules struc-
turally related to it, such as carboxyl sulfide, carbon disulfide, ketene, thioketene, hydrogen isocyanate, and hydrogen isothiocyanate. We have used the model metallic fragment Fe(CO)$_2$(PH$_3$)$_2$ as the basic system for the cumulene molecules. This choice is justified by the well-characterized related complex Fe(CO)$_2$(PMe$_3$)(PPh$_3$)(q$^2$-CS$_2$).$^{12}$

The systems Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-OCX) and Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-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$^{22}$ was used for the phosphorus atoms and the carbonyl groups, and a (2s) contraction was used for the saturated ligand. 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, OCN$_2$, OCCH$_2$, CS$_2$, SCNH, and SCCH$_2$, Dunning's basis set$^{27,28}$ of double-$	au$ quality was employed. All geometrical optimizations described herein were carried out by using this basis. Subsequent single-point calculations of the optimized structures were performed by using the extended basis II. Here the s-p basis for iron was taken from the (12s6p4d) set of ref 29, with the addition of two functions to describe the 4p orbital, while the Fe d basis was the reoptimized (5d) set of ref 31, contracted (4/1). This leads to an (118s5p5d) primitive basis for iron, contracted (6s6p2d). The same double-$	au$ set$^{27,28}$ was employed in basis II 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 of the interaction of iron and formaldehyde.$^{32}$ In particular, the basis set superposition error has been evaluated according to Boys and Bernardi$^{11,12}$ and found to be acceptably small ($3.9 \text{ kcal mol}^{-1}$ with basis I, $4.6 \text{ kcal mol}^{-1}$ with basis II). "Ab initio" spin-restricted Hartree-Fock SCF gradient calculations were performed in partial geometry optimizations of the complexes Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-CO$_2$), Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-COS), Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-OCNH), Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-OCCH$_2$), Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-SCNH), Fe(CO)$_2$(PH$_3$)$_2$(q$^2$-SCCH$_2$) and in deriving estimates of the binding energies of all the molecules with respect to the free OCX or SCX (with X = O, S, NH, CH$_2$) and the iron-frAGMENT species. Dissociation of these fragments may lead to either singlet or triplet products in triplet.

**References**

The geometry of the Fe(CO)$_2$(PH$_3$)$_2$(OCCH$_2$) group has been taken from ref 32 and is in reasonable agreement with the experimental structure of Cp$_2$V(q$_2$-SCNPh) (C-0, 1.29 A; C-C, 1.34 A; Zr-C-C, 135.9$^\circ$) and the optimized structure of Fe(CO)$_2$(PH$_3$)$_2$(OCCH$_2$)$_2$ (SCNPh) is in line with the experimental one of (C$_2$H$_5$)$_2$V(q$_2$-SCNPh) (C-S, 1.745 A; C-N, 1.265 A; Zr-C-N, 138.6$^\circ$).

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 the true binding 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 OCX (or SCX) to be monodentate or bidentate and of the interaction energy (INT) resulting from the interaction between the iron fragment and the distorted ligand. 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$_3$)$_2$-OCCH$_2$ is larger than that of the other three complexes, its interaction energy is comparable to that of the OCCH$_2$ compound, whose net binding energy is substantially lowered by the relatively high energy required for OCCH$_2$ deformation. In contrast, COS exhibits a small interaction energy.

Table I. Partially Optimized Geometries of the Systems under Investigation$^a$

<table>
<thead>
<tr>
<th></th>
<th>Fe-C</th>
<th>Fe-O</th>
<th>C=S</th>
<th>C-S</th>
<th>ZO-C-O</th>
<th>Z-C-Fe-CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-C</td>
<td>1.983</td>
<td>2.335</td>
<td>1.676</td>
<td>1.615</td>
<td>138.9</td>
<td>92.3</td>
</tr>
<tr>
<td>Fe-S</td>
<td>1.857</td>
<td>2.457</td>
<td>1.767</td>
<td>2.020</td>
<td>138.0</td>
<td>94.3</td>
</tr>
<tr>
<td>C-S</td>
<td>1.460</td>
<td>1.857</td>
<td>1.767</td>
<td>2.020</td>
<td>138.0</td>
<td>94.3</td>
</tr>
<tr>
<td>ZS2-C</td>
<td>1.138</td>
<td>1.380</td>
<td>1.302</td>
<td>1.202</td>
<td>138.0</td>
<td>94.3</td>
</tr>
<tr>
<td>Z-C-Fe-CO</td>
<td>1.857</td>
<td>2.457</td>
<td>1.767</td>
<td>2.020</td>
<td>138.0</td>
<td>94.3</td>
</tr>
</tbody>
</table>

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

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 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 is y-bonded to the metal. The M-C and M-O bond lengths are respectively 1.84 and 1.99 A in [Ni(PC$_3$)$_3$(OH)(CO)$_2$]OH$_2$; 2.112 and 2.190 A in [Ni(C$_5$H$_6$)(OMe)(OCOMe)$_2$]OMe; 2.144 and 2.173 A in [Ni(bis(1,1-dimethylallyl)amine)(CO)$_2$]OMe; 2.105 and 2.147 A in [Mn(C$_5$H$_5$)(CN)(PMe$_3$)(CN$_2$)]$_2$. The computed C-O bond lengths vary between 1.230 and 1.275 A, and these values are always longer than those exhibited by the free ligands (CS$_2$, 1.55 A; COS, 1.56 A; SCN$_2$, 1.57 A; SCCH$_2$, 1.55 A). 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(q$_2$-OCCPh)$_2$ (C-O, 1.29 A; C-C, 1.34 A; Zr-C-C, 135.9$^\circ$) and the optimized structure of Fe(CO)$_2$(PH$_3$)$_2$(OCCH$_2$)$_2$ (SCNPh) is in line with the experimental one of (C$_2$H$_5$)$_2$V(q$_2$-SCNPh) (C-S, 1.745 A; C-N, 1.265 A; Zr-C-N, 138.6$^\circ$).

References:

energy, comparable to that of CO, 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, compared to those of OCNH and OCCH,, and the higher deformation energy of CO, 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.

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(PH3)2(\pi-CO2) with those of the singlet fragments, where only the main correlations are reported. To emphasize the effects of CO2 distortion upon complex formation, Figure 1 also shows the orbital energy levels of free CO, both at its equilibrium geometry and at the C$_2$ 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 CO2 group. The 37a' and 38a' molecular orbitals originate from the interaction of the Fe(CO)2(PH3)2 19a, and CO2 9a'(\pi) filled orbitals. This is a four-electron destabilizing interaction. Effective bonding, therefore, is concentrated in the 39a' orbital (hereafter denoted as d$_{\pi}$) and the virtual orbital of CO2 10a'(2\pi) (hereafter denoted as \pi*). The former orbital is mainly iron d$_{\pi}$ in character (the Fe–CO2 moiety lies in the xy plane). Thus, the main bonding interaction is the \pi back-donation from the metal atom to the unsaturated ligand. Figure 1 shows also that the CO2 distortion upon coordination lowers the \pi* orbital energy and reduces the gap between this orbital and the fragment d$_{\pi}$ orbital. The distortion of CO2 implies therefore an increased \pi 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(PH3)2 d$_{\pi}$ and the ligand \pi* orbitals. The main bonding interaction in all the systems under investigation is thus the \pi 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.
The results of Table III show that the coordination of OCX implies a flow of electron density from the ligands CO and PH₃ 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 CO₂, and 0.28 e for OCCH₂) when using basis II than when using basis I. This suggests the presence of a small ligand-to-metal φ-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 φ-donative interaction should strongly involve the empty iron 4p orbital, which is satisfactorily described by basis II but not by basis I. As can be seen from Table
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}((\&OCC\{\{C\}}), when basis II is used. We notice that a better described \( \sigma \) 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 \( \sigma \) and \( \pi \) interactions between the metal fragment and the carbonyl and phosphine ligands, implying an overall stronger competition toward coordination between these ligands and the \( \pi^{2}-C,O \)-bonded heterocumulene molecules.

The strength of the \( \pi \) back-donation can be related to the \( \pi^{*} \)-orbital energy of the OCX ligand. A lower \( \pi^{*} \) energy implies a smaller energy gap between this orbital and the filled \( \delta_{a} \) 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 \( \pi^{*} \) orbital. The \( \pi^{*} \) energy is computed to be 0.2167, 0.1723, 0.1162, and 0.1084 \( \text{au} \) for free (undistorted) OCNH, CO, OCCH_{2}, and COS, respectively, and decreases to 0.0069, 0.0055, 0.0281, and -0.0099 \( \text{au} \), respectively, upon distortion. These values suggest that the \( \pi \) back-donation increases in the order OCCH_{2} < OCNH < CO < COS. This trend cannot be directly related with the interaction energy, which increases in the order CO < COS ≪ OCCH_{2} ≈ 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 ≈ CO_{2} ≪ 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}((\&OCC\{\{C\}}) and a very high delocalization (69%) on the S atom in the bonding orbital of Fe(CO)_{2}(PH_{3})_{2}(\pi^{2}-COS). Therefore, the bond between the iron fragment and the COS molecule is not as strong as one could expect by considering just the \( \pi \) backdonation since there is a high delocalization of the electron density on the sulfur atom, while in Fe(CO)_{2}(PH_{3})_{2}(\pi^{2}-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 ≪ OCCH_{2} ≈ OCNH can be explained by taking into account at the same time the strength of the \( \pi \) 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}(\pi^{2}-COS) has a high nucleophilic character and, therefore, this compound should undergo alkylidene very easily. On the other hand, the compound with ketene should present a different reactivity, in agreement with the experimental evidence that Cp_{2}Zr((\pi^{2}-OCCH_{2})CH_{2}Na-2THF reacts with CH_{2}I, even under drastic conditions.\(^{10}\) [Cp_{2}Zr((\pi^{2}-OCCH_{2})CH_{2}Na-2THF reacts with CH_{2}I, but the NMR spectroscopic and structural data do not indicate a high negative charge density at the CH_{2}I group.]\(^{10}\)

**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 \( \pi \) back-donative interaction between the iron \( \delta_{a} \) orbital and the \( \pi^{*} \) orbital of the unsaturated ligand.

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 \( \text{e} \) for SCNH, 0.29 \( \text{e} \) for COS, 0.30 \( \text{e} \) for CS_{2}, and 0.34 \( \text{e} \) 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 \( \sigma \)-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 \( \pi \) and nonbonding orbital energies of the SCX ligands (not reported in the tables) result to be systematically about 0.1 \( \text{au} \) 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 \( \pi \) 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 \( \pi^{*} \) orbital energies of the deformed ligands, reported in Table III.

It is interesting to note that the \( \pi^{*} \) energy of COS, which is -0.0099 \( \text{au} \) for COS at the distorted geometry of the compound where it is \( \pi^{2}-C,O \)-bonded, is lowered to -0.0137 \( \text{au} \) when COS is \( \pi^{2}-C,S \)-bonded to the iron. Therefore, the \( \pi^{2}-C,S \) coordination of the carbonyl sulfide is preferred, with respect to the \( \pi^{2}-C,O \) mode, because of the increased \( \pi \) back-donation, in agreement

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

<table>
<thead>
<tr>
<th>Ligand</th>
<th>CO_{2}</th>
<th>COS</th>
<th>OCNH</th>
<th>OCCH_{2}</th>
<th>CO_{2}</th>
<th>COS</th>
<th>CS_{2}</th>
<th>SCNH</th>
<th>SCCH_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orbital energy</td>
<td>39a'</td>
<td>42a'</td>
<td>39a'</td>
<td>42a'</td>
<td>42a'</td>
<td>45a'</td>
<td>42a'</td>
<td>42a'</td>
<td>42a'</td>
</tr>
<tr>
<td>Fe</td>
<td>36</td>
<td>17</td>
<td>34</td>
<td>38</td>
<td>29</td>
<td>17</td>
<td>26</td>
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<tr>
<td>C</td>
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<td>14</td>
<td>18</td>
<td>12</td>
<td>9</td>
<td>13</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>X</td>
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<td>6</td>
<td>14</td>
<td>18</td>
<td>12</td>
<td>9</td>
<td>13</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Y</td>
<td>25</td>
<td>69</td>
<td>24</td>
<td>8</td>
<td>4</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

\( ^{a} \) \( \pi^{2}-C,O \)-bonded. \( ^{b} \) \( \pi^{2}-C,S \)-bonded. \( \chi = O. \) \( \chi = S. \) \( \chi = \text{NH}. \) \( \chi = CH_{2}. \)
with the experimental evidence that no $\pi^2$-C=S bond is present in the systems Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-OCX) and Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-SCX) (with X = O, S, NH, CH$_3$) has shown that the main bonding interaction between the fragment Fe(OC)$_2$(PH$_3$)$_2$ and the unsaturated molecule is the $\pi$ back-donation from the transition metal to the $\pi$-acceptor ligand and the strength of this coordination bond increases on going from OCX to SCX. Moreover, the $\pi$ back-donation is the driving force of the ligand deformation, which allows a better overlap between the $\pi^*$ ligand and the d$_z^2$ 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 $\pi$ acidity exhibited by this molecule. The preference of the carbonyl sulfide for the $\pi^2$-C=S coordination can be explained in the same context: this coordination bonding mode is preferred, with respect to the $\pi^2$-C=S mode, because of the increased $\pi$ back-donation, in agreement with the experimental evidence that no $\pi^2$-C=S bond is present in these systems.

In the two analyzed series of compounds of Fe(OC)$_2$(PH$_3$)$_2$, with OCX and SCX, the delocalization of electron density on the heterogroup increases on going from X = CH$_3$ 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$_3$ group in the compounds with ketene and thioketene should not undergo alkylation very easily.

### Acknowledgment

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### Registry No.

Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-OCO$_2$), 110174-28-2; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-CSO$_2$), 110174-29-3; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-OCNH), 110174-30-6; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-OCCH$_2$), 110174-31-7; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-CS$_2$), 110174-32-8; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-CSO$_2$), 110174-34-0; Fe(OC)$_2$(PH$_3$)$_2$($\sigma^2$-SCN), 110174-35-1; Fe, 7439-89-6.

### Notes

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**Reactions of the Dirhenium(III) Carboxylate Complexes**

Re$_2$(O$_2$CR)$_2$X$_2$L$_2$ (R = Me, Et; X = Cl, Br; L = H$_2$O, py, 4-Mepy, DMF, Me$_2$SO, Ph$_3$PO) have been known for several years and their syntheses, structures, and spectroscopic properties are quite well documented,$^{1-3}$ an examination of their chemical reactivity has been largely neglected. Recently, we have studied the reactions of several complexes of the type Re$_2$(O$_2$CR)$_2$X$_2$L$_2$ (X = Cl, Br; R = Me, Et; L = CH$_3$CO, py, DMF, Me$_2$SO) with monodentate tertiary phosphines in alcohol solvents.$^{4,5}$ Whereas Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$L$_2$ (L = H$_2$O, py) react with PMe$_3$, PMe$_2$Ph, and PMePh$_2$ to give the dirhenium(II) complexes Re$_2$L$_2$(PH$_3$)$_4$, the novel dirhenium(IV,II) alkoxide complexes (R'O)$_2$ReReCl$_2$(PH$_3$)$_4$ were produced in the reactions between Re$_2$(O$_2$CR)$_2$X$_2$L$_2$ (X = Cl, Br; R = Me, Et; L = H$_2$O, DMF, Me$_2$SO) and PPh$_3$ in refluxing alcohol solvents R'OH (R' = Me, Et, n-Pr, i-Pr).$^{4,5}$ During the course of these reactions we have noted that the reactions between Re$_2$(O$_2$CCH$_3$)$_2$Cl$_2$L$_2$ (L = py, 4-Mepy) and PPh$_3$ in refluxing ethanol did not yield (EtO)$_2$Cl$_2$ReReCl$_2$(PH$_3$)$_4$. 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$_2$CCH$_3$)$_2$Cl$_2$(PH$_3$)$_4$. The chemistry of this and related systems is described in the present report.

**Experimental Section**

**Starting Materials.** The compounds (n-Bu$_4$N)Re$_2$L$_2$ (X = Cl, Br) were synthesized as described in the literature.$^{6,7}$ These were converted

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