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Interaction between Iron(0) and Formaldehyde, Thioformaldehyde, and Acetone: "Ab Initio" Calculations on the Model Compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$

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"Ab initio" calculations have been performed on the model systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ to investigate the nature and the energetics of the interaction between iron and formaldehyde, thioformaldehyde, and acetone. The results allow a complete description of the electronic structure of the model compounds: the coordinate bond between the iron fragment and the unsaturated molecule may essentially be described in terms of the π-back-donation from the transition metal to the π-acceptor ligand. Partial geometry optimizations obtained by gradient calculations show that the geometry of the coordinated ligand is greatly distorted and the deformation upon coordination is satisfactorily reproduced when a comparison with experimental data is available. Thioformaldehyde gives rise to a stronger bond with iron than formaldehyde, because it is found to be a better π-acceptor ligand and a better σ-donor ligand. The π-back-donations are comparable in $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$, but acetone exhibits a weaker bond with iron than formaldehyde since it requires a higher deformation energy.

Introduction

The interaction between transition-metal complexes and formaldehyde has been experimentally studied in the last few years[1–8] since the presence of a metal–formaldehyde complex has been postulated to be a pivotal intermediate in the catalytic activation of carbon monoxide.[9–13] An important contribution should be the understanding of the interaction of CH_2O formed formally from a mixture of $CO + H_2$ with a metal site. A structural model for such an event may be the interaction of a carbonyl group with a metal site.

The interaction of CH_2O with a metal site has usually been described by two limiting schemes: either a metal–cyclopropane scheme[14] or the olefin-type Chatt–Dewar–Duncanson model[15] involving ligand to metal σ-donation and metal to ligand back-donation. Recent "ab initio" theoretical studies[16,17] suggest, however, that neither of these models seems appropriate, since the metal uses essentially a single orbital in a back-donation interaction with CH_2O. In addition, the driving force for the distortion of the formaldehyde resides in the enhanced back-donative stabilization thus obtained. The presence of electron-donor ligands coordinated to the transition metal increases the electron density at the metal center and, therefore, the π-back-donation and the strength of the $M\text{–}CH_2O$ bond.

In this paper we intend to investigate, via "ab initio" calculations, the interaction between iron, a metal that plays an important role as catalyst in the Fischer–Tropsch synthesis,[10–13] and formaldehyde, thioformaldehyde, and acetone. The main objective of the present study is the evaluation of the critical factors affecting the $M(C{=}X)$ interaction in terms of energetic balance, namely (a) the nature of the heteroatom (X), (b) the substituents at the carbon, which can affect both the electron-withdrawing properties and the changes in geometry required for enabling coordination to the metal, and (c) the critical ligand substitution at the metal.

For this purpose, we have studied the complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ (Me = CH_3). The first one has an experimental counterpart, that is $Fe(CO)_2[P(OCH_3)_3]_2(\eta^2\text{-}CH_2O)$, a well-characterized species,[4] while the other three are assumed to be model complexes, for the purpose of comparison of the coordinate bond of CH_2O with those of CH_2S and CMe_2O. The more basic fragment "$Fe(PH_3)_4$" has been considered for the interaction with acetone, since a bond weaker than those of CH_2O and CH_2S is expected for this molecule.[1]

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[18] by splitting the outermost s and d functions. The MINI-1 basis[19,20] was used for the phosphorus atoms and the carbonyl groups, and a (2s) contraction[19] of Van Duijneveldt's (4s) primitive set[21] was adopted for the phosphine hydrogens. For the component atoms of formaldehyde, thioformaldehyde, and acetone, Dunning's basis set[22,23] of double-ζ quality was employed. All geometry optimizations described herein were conducted by using this basis. Subsequent single-point SCF calculations at the optimized geometries were performed for the compounds $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, by using the more extended basis II (but not for the largest system, $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$, due to the size of the problem). Here the s,p basis for iron was taken from the (12s6p4d) set of ref 24 with the addition of two basis functions to describe the 4p orbital,[25] while the Fe d basis was the reoptimized (5d) set of ref 26, contracted (4/1). This leads to an (11s8p5d) primitive basis

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(1) Clark, G. R.; Headford, C. E. L.; Marsden, K.; Roper, W. R. *J. Organomet. Chem.* **1982**, *231*, 335.

(2) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1982**, *104*, 2019. (b) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1986**, *5*, 2425.

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

(4) (a) Berke, H.; Bankhardt, W.; Huttner, G.; Von Seyerl, J.; Zsolnai, L. *Chem. Ber.* **1981**, *114*, 2754. (b) Berke, H.; Huttner, G.; Weiler, G.; Zsolnai, L. *J. Organomet. Chem.* **1981**, *219*, 353.

(5) Head, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1637.

(6) Green, M. L. H.; Parkin, G.; Moynihan, K. J.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1984**, 1540.

(7) Buhro, W. E.; Patton, A. T.; Strouse, C. E.; Gladysz, J. A.; McCormick, F. B.; Etter, M. C. *J. Am. Chem. Soc.* **1983**, *105*, 1056.

(8) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 1690.

(9) Dombek, B. D. *J. Am. Chem. Soc.* **1980**, *102*, 6855.

(10) Henrici-Olivé, G.; Olivé, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136.

(11) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117.

(12) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479.

(13) Rofer DePoorter, C. K. *Chem. Rev.* **1981**, *81*, 447.

(14) Conway, P.; Grant, S. M.; Manning, A. R. *J. Chem. Soc., Dalton Trans.* **1979**, 1920.

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

(16) Sakaki, S.; Kitaura, K.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1983**, *22*, 104.

(17) Rosi, M.; Sgamellotti, A.; Tarantelli, F.; Floriani, C.; Guest, M. F. *J. Chem. Soc., Dalton Trans.*, in press.

(18) Tatewaki, H.; Sakai, Y.; Huzinaga, S. *J. Comput. Chem.* **1981**, *2*, 278.

(19) Tatewaki, H.; Huzinaga, S. *J. Comput. Chem.* **1980**, *1*, 205.

(20) Sakai, Y.; Tatewaki, H.; Huzinaga, S. *J. Comput Chem.* **1981**, *2*, 100.

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

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

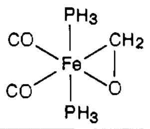
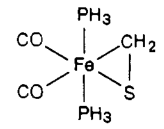
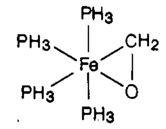
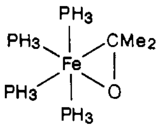
(23) Dunning, T. H., Jr.; Hay, P. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 4, p 1.

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

(25) Hood, D. M.; Pitzer, R. M.; Schaefer, H. F., III. *J. Chem. Phys.* **1979**, *71*, 705.

0020-1669/88/1327-0069$01.50/0

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

							
Fe–C	1.952 (2.03)[c]	Fe–C	1.957	Fe–C	1.900	Fe–C	1.988
Fe–O	1.971 (2.00)[c]	Fe–S	2.325	Fe–O	1.917	Fe–O	1.868
C–O	1.311 (1.32)[c]	C–S	1.815	C–O	1.354	CO	1.375
C–H	1.082	C–H	1.078	C–H	1.087	$C-C_{Me}$	1.552
∠C–Fe–CO	102.1 (108.5)[c]	∠C–Fe–CO	89.7	$\angle C-Fe-PH_3$	110.1	$\angle C-Fe-PH_3$	118.1
∠H–C–H	112.4	∠H–C–H	110.7	∠H–C–H	110.5	$\angle C_{Me}-C-C_{Me}$	109.0
$\angle\alpha$[b]	29.1	$\angle\alpha$	40.3	$\angle\alpha$	37.3	$\angle\alpha$	49.2
						$C_{Me}-H$	1.086
						$\angle H-C_{Me}-C$	112.2

[a] Bond lengths are in angstroms and bond angles in degrees. [b] α is the distortion angle, defined as the angle between the CH_2 plane and the C–O bond in the formaldehyde compound. [c] Experimental values relative to $Fe(CO)_2[P(OCH_3)_3]_2(\eta^2\text{-}CH_2O)$.

for iron, contracted (8s6p2d). A double-ζ expansion was used for all ligand atoms, with a (4s/2s) basis for hydrogen,[22] a (9s5p/4s2p) contraction for carbon and oxygen,[22] and an (11s7p/6s4p) contraction for phosphorus and sulfur.[23,27]

The basis set superposition error has been calculated as proposed by Boys and Bernardi[28] for the complex $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. Basis I and basis II values of 3.9 and 4.6 kcal·mol^{-1}, respectively, suggest that our results should not be unduly affected by superposition errors.

"Ab initio" spin-restricted Hartree–Fock gradient calculations were used in partial geometry optimizations of the four complexes $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ and in deriving estimates of the binding energies of all complexes with respect to the free unsaturated ligand and the fragment species.

It is well-known that correlation effects may affect substantially the description of systems with transition-metal atoms. Configuration interaction calculations, carried out on the complex $Fe(CO)_4(\eta^2\text{-}CH_2O)$ and the separated fragments CH_2O and $Fe(CO)_4$,[17] have clarified, however, that the correlation effects do not markedly influence the energetics of bond formation between Fe and CH_2O, so that the interaction energies computed at the Hartree–Fock level appear to be satisfactorily reliable.

In the case of the formaldehyde complex, we have already addressed[17] the question of whether dissociation would lead to singlet or triplet products. At the Hartree–Fock level of theory, the fragments $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$ are predicted to have a triplet ground state, but as has been found in the case of iron–tetracarbonyl through configuration interaction calculations,[17] the relative energy of the first singlet state is expected to decrease drastically upon inclusion of correlation effects and possibly become the true ground state. The high energy gap between the singlet ground state and the first excited state of CH_2O, CH_2S, and CMe_2O (71.9,[29] 41.5,[30] and >88 kcal·mol^{-1},[29] respectively) should therefore be decisive in driving the dissociation process toward singlet products. Accordingly, all our calculations refer to the investigated species in their lowest singlet state.

All computations were performed by using the GAMESS program package,[31] 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 formaldehyde, thioformaldehyde, and acetone, an approach consistent with the experimental structure of the transition-metal complexes involving formaldehyde or thioformaldehyde.[1-7,32] End-on coordination has been observed for the acetone molecule in $[Cp_2V(CMe_2O)]^+(BPh_4)^-$,[33] where the high positive charge on the vanadium atom favors the electrostatic interaction over the π-back-donation. The Fe(0) unsaturated fragments $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$ have a strong Lewis basicity, and therefore, only side-on coordination should be attainable for them. In the partial geometry optimization calculations we have optimized the geometrical parameters involving the iron atom and the atoms of the formaldehyde and formaldehyde-derived ligands. The geometries of the $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$ groups have been kept fixed at the values appropriate to the formaldehyde complexes, as described in ref 17. No geometry optimization has been performed for the dissociated species: the geometries of the $Fe(CO)_2(PH_3)_2$ and $Fe(PH_3)_4$ fragments have been taken equal to those in the complexes, while the experimental geometries[34] have been used for CH_2O,[35] CH_2S,[36] and CMe_2O.[37] The optimized structures of the com-

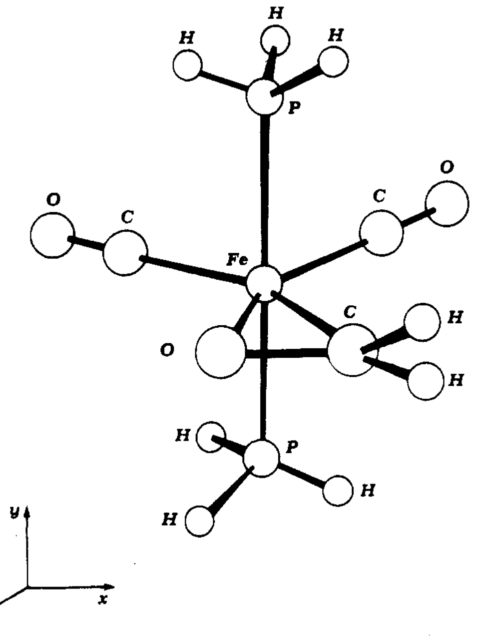


Figure 1. Optimized geometry of the model system $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. Bond lengths and angles are reported in Table I.

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(26) Rappe, A. K.; Smedley, T. A.; Goddard, W. A., III. *J. Phys. Chem.* **1981**, *85*, 2607.

(27) The influence of a d polarization function added to the basis set of the sulfur atom (exponent 0.542: Ahlrichs, R.; Taylor, P. R. *J. Chim. Phys. Phys.-Chim. Biol.* **1981**, *78*, 315) has been checked on the π and π^* orbital energies of free CH_2S. The π and π^* energies of the deformed ligand with (and without) the d function are respectively –0.3820 (–0.3855) and 0.0020 au (–0.0019 au). No d functions were then included in the sulfur basis set.

(28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(29) Herzberg, G. *Electronic Spectra and Electronic Structure of Polyatomic Molecules*; Van Nostrand: New York, 1966.

(30) Pope, S. A.; Hillier, I. H.; Guest, M. F. *J. Am. Chem. Soc.* **1985**, *107*, 3789.

(31) (a) Dupuis, M.; Spangler, D.; Wendolowski, J. *NRCC Software Catalog*; National Resource for Computation in Chemistry, Lawrence Berkeley Laboratory, University of California: Berkeley, CA, 1980; Vol. 1, Program No. QG01 (GAMESS). (b) Guest, M. F.; Kendrick, J. "GAMESS User Manual"; Daresbury Technical Memorandum; Daresbury Laboratory: Daresbury, England, 1985.

(32) Collins, T. J.; Roper, W. R. *J. Organomet. Chem.* **1978**, *159*, 73.

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

(34) The molecular geometries of free CH_2O, CH_2S, and CMe_2O have been optimized: bond lengths and angles are predicted accurate to approximately 0.01–0.02 Å and 1°, respectively. The differences in total energies between experimental and optimized geometries are small: 0.9, 0.6, and 0.8 kcal·mol^{-1} for CH_2O, CH_2S, and CMe_2O, respectively.

(35) Oka, T. *J. Phys. Soc. Jpn.* **1960**, *15*, 2274.

(36) Johnson, D. R.; Powell, F. X.; Kirchhoff, W. H. *J. Mol. Spectrosc.* **1971**, *39*, 136.

plexes under investigation are shown in Table I. For the sake of clarity, the structure of the complex $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ in its optimized geometry, including the coordinate system, has been reported in Figure 1. Each compound 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 CH_2O, CH_2S, or CMe_2O to be monodentate or bidentate. The iron atom is bonded to two mutually trans phosphines in the axial sites and to two carbonyls (or two phosphines) and the unsaturated molecule in the equatorial sites. A comparison with experimental data is possible only for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, which is a model system for the well-characterized compound $Fe(CO)_2[P(OCH_3)_3]_2(\eta^2\text{-}CH_2O)$.[4] The distortion of the formaldehyde molecule upon coordination is satisfactorily reproduced. In particular, the experimentally observed elongation of the C–O distance on bonding, from 1.21 to 1.32 Å, is accurately predicted (1.311 Å in the optimized structure), while the distortion angle, defined as the angle between the CH_2 plane and the C–O bond, is calculated to be 29.1°. This value is in line with the experimental angle of 26.6° found in the nickel complex $Ni(PEt_3)_2(\eta^2\text{-}CPh_2O)$.[38] The iron–formaldehyde bond is experimentally found to be very slightly asymmetric, with the Fe–C distance (2.03 Å) longer than the Fe–O distance (2.00 Å). Our partially optimized structure satisfactorily reproduces the absolute values of these bond distances (1.952 Å for Fe–C and 1.971 Å for Fe–O), although the slightly greater deviation from experiment of the Fe–C distance causes an inversion in their relative magnitudes. The calculated ∠C–Fe–O angle of 39.0°, obtainable from the values in Table I, is in excellent agreement with the experimental estimate of 38.2°.

The system $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ is computed to have shorter Fe–C and Fe–O bond lengths compared with those exhibited by $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ (Fe–C, 1.900 Å; Fe–O, 1.917 Å), and this suggests the presence of a stronger interaction. In addition, the distortion of the formaldehyde molecule is more pronounced in the tetrakis(phosphine) compound. Considering now the thioformaldehyde complex, we see that in the optimized structure the Fe–C distance (1.957 Å) is very close to the value found in the corresponding formaldehyde compound. However, thioformaldehyde itself undergoes a stronger geometry change than CH_2O upon coordination: the deviation from planarity is 40.3°, and the elongation of the C–S distance relative to that in free CH_2S is about 0.2 Å. It is interesting to note that the resulting C–S distance of 1.815 Å is typical of a C–S single bond (1.81–1.82 Å)[39a] and substantially longer than that observed in other CH_2S complexes (1.742[7] and 1.762 Å[40] in $[(C_5H_5)Re(NO)(PPh_3)(\eta^2\text{-}CH_2S)]^+(PF_6)^-$ and $Cp_2V(\eta^2\text{-}CPh_2S)$, respectively). The presence of a C–Se single bond has been experimentally observed in the μ,η^2-selenoformaldehyde complex $(\eta^5\text{-}C_5R_5)_2Mn_2(CO)_4(CH_2Se)$;[41] in this compound, however, selenoformaldehyde functions as a bridging ligand. Finally, we may comment briefly on the optimized structure of $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$. In this case the presence of the two methyl groups causes an increase of ~0.09 Å in the Fe–C bond length and a decrease of 0.05 Å in the Fe–O distance, with respect to those in the corresponding CH_2O complex. As a result, the Fe–O distance is now noticeably shorter (by 0.12 Å) than the Fe–C distance. Furthermore, the acetone distortion angle is expectedly larger than the CH_2O one. A comparable C–O bond elongation is instead observed in the two complexes (the C–O distance in free acetone is 1.222 Å),[37] which results in a C–O bond length somewhat intermediate between that of the free ligand and that typical of a C–O single bond (1.41–1.43 Å).[39b]

Results and Discussion

The total SCF energies of the four complexes investigated and of their related free fragments are reported in Table II, together with the estimated binding energies. The binding energies have been computed as the differences between the energies of the complexes and the energies 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 fragments, we expect our data to somewhat overestimate (in absolute value) the true fragmentation energies of the complexes. However, this should not affect the main qualitative conclusions of our comparative analysis.

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

complex	total SCF energies basis I	total SCF energies basis II
$Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$	−2276.7033	−2285.9449
$Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$	−2599.3666	−2608.6252
$Fe(PH_3)_4(\eta^2\text{-}CH_2O)$	−2734.3141	
$Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$	−2812.3495	

fragment	total SCF energies basis I	total SCF energies basis II
$Fe(CO)_2(PH_3)_2$	−2162.8254	−2172.0633
$Fe(PH_3)_4$	−2620.3905	
CH_2O	−113.8293	−113.8293
CH_2S	−436.4578	−436.4578
CMe_2O	−191.9004	

complex		binding energies basis I	binding energies basis II
$Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$	INT	−45.9	−48.2
	DEF	15.4	15.4
	BE	−30.5	−32.8
$Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$	INT	−76.0	−89.0
	DEF	23.7	23.7
	BE	−52.3	−65.3
$Fe(PH_3)_4(\eta^2\text{-}CH_2O)$	INT	−86.7	
	DEF	27.5	
	BE	−59.2	
$Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$	INT	−87.6	
	DEF	50.8	
	BE	−36.8	

[a] See text.

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.[16] The deformation and interaction energies are also reported in Table II.

Comparative Study of the Iron–Formaldehyde and Iron–Thioformaldehyde Bonds. As can be seen in Table II, the binding energy of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$ is computed to be substantially larger than that of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, indicating that CH_2S is capable of a stronger interaction with iron than CH_2O. As we have seen, the distortion of thioformaldehyde upon coordination is more pronounced than that of formaldehyde and, correspondingly, a higher deformation energy is computed (23.7 kcal·mol^{-1} for CH_2S and 15.4 kcal·mol^{-1} for CH_2O). However, the higher energy required for the distortion of CH_2S is more effectively compensated by the much larger interaction energy. It is interesting to note that upon extension of the basis set on the iron substrate from basis I to basis II the interaction energy for CH_2O does not vary appreciably, while the interaction energy for CH_2S increases substantially (by 13 kcal·mol^{-1}). This suggests the presence of a source of interaction, which basis II describes better than basis I, and which is more effective for coordination of CH_2S than for coordination of CH_2O. This point will be further analyzed below.

To understand qualitatively the nature of the coordination bond between the iron substrate and the CH_2X ligand (X = O, S), it is useful to analyze the correlation between the molecular orbitals of the complex and those of the free fragments. Figure 2 shows such a correlation diagram for the orbitals of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and those of the singlet fragments, where only the main correlations are reported. The orbitals mainly involved in the iron–formaldehyde bonding are 33a′, 35a′, and 36a′. The 33a′ and 35a′ molecular orbitals originate from the interaction of the filled orbitals $19a_1$ from $Fe(CO)_2(PH_3)_2$ and $1b_1$ from CH_2O. This

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(37) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. *J. Phys. Chem. Ref. Data* **1979**, *8*, 619.

(38) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311.

(39) (a) Streiwieser, A., Jr.; Heathcock, C. H. *Introduction to Organic Chemistry*, 2nd ed.; Macmillan: New York, 1981; p 807. (b) Ibid., pp 229–230.

(40) Pasquali, M.; Leoni, P.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1983**, *22*, 841.

(41) Herrmann, W. A.; Weichmann, J.; Serrano, R.; Blechschmitt, K.; Pfisterer, H.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 314.

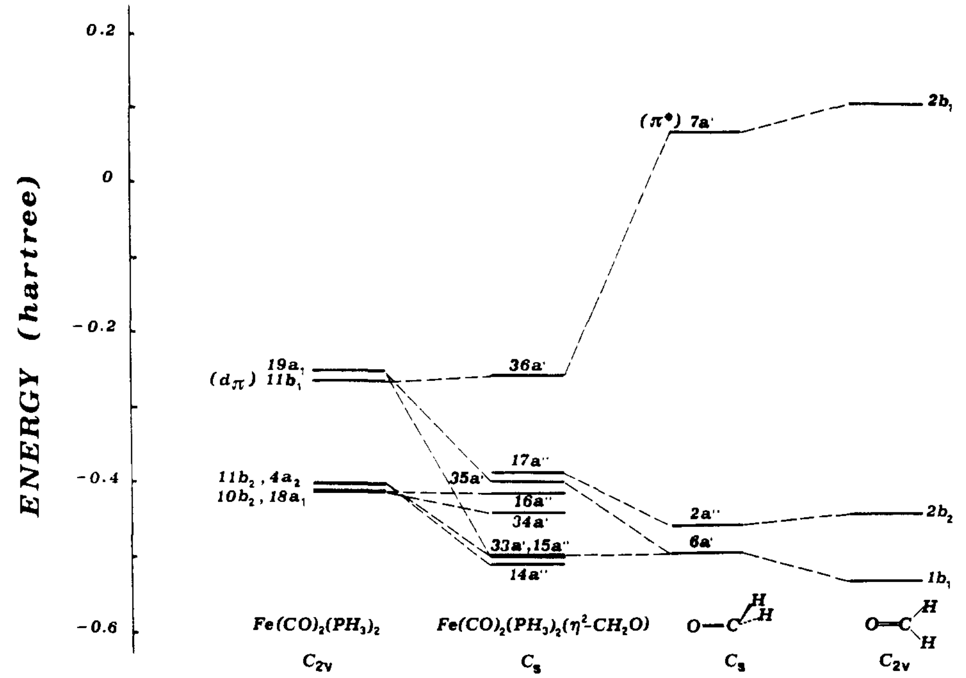

Figure 2. Molecular orbital correlation diagram of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. For clarity's sake, only the main correlations are reported.

Table III. Mulliken Population Analysis of the Investigated Systems and π- and π*-Orbital Energies (hartree) of the Deformed Ligands

	$Fe(CO)_2(PH_3)_2$		$Fe(CO)_2(PH_3)_2$-(η^2-CH_2O)		$Fe(CO)_2(PH_3)_2$-(η^2-CH_2S)		$Fe(PH_3)_4$	$Fe(PH_3)_4(\eta^2\text{-}CH_2O)$	$Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$
	basis I	basis II	basis I	basis II	basis I	basis II	basis I	basis I	basis I
Fe s	5.94	6.26	5.87	6.35	5.91	6.38	5.96	6.00	6.02
p	11.99	12.64	12.00	12.65	12.00	12.79	12.00	12.01	12.01
d	7.47	7.23	7.30	7.17	7.14	7.15	7.76	7.19	7.11
ax ligands	36.00	35.61	35.96	35.48	35.86	35.40	36.12	36.00	36.02
eq ligands	28.60	28.26	28.34	27.88	28.24	27.78	36.16	35.97	35.94
L[a]			16.53	16.47	24.85	24.50		16.83	32.90
π energy			−0.4980		−0.3855			−0.4856	−0.4392
π* energy			0.0677		−0.0019			0.0507	0.0582

[a] L is the unsaturated ligand: formaldehyde, thioformaldehyde, or acetone.

is a four-electron destabilizing interaction. Effective bonding, therefore, is concentrated in the 36a′ orbital, which is the bonding combination of $11b_1$ of $Fe(CO)_2(PH_3)_2$ (hereafter denoted as d_π), which is predominantly Fe d_{xz} in character (the Fe—η^2-C,O moiety lies in the xz plane), and the virtual orbital $2b_1$ of CH_2O (hereafter denoted as π*). Clearly the main bonding interaction between iron and formaldehyde is the π-back-donation from the transition metal to the ligand, while the $CH_2O \rightarrow$ Fe σ-donation is almost absent. This picture is substantiated on performing a localization of the molecular orbitals by using the Foster–Boys algorithm.[42] The resulting localized molecular orbitals reveal that effective bonding between iron and formaldehyde is concentrated in a single localized molecular orbital, featuring overlap of the metal $3d_{xz}$ and the formaldehyde π* orbitals.

$Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$ shows the same bonding picture: the main bonding orbital is 39a′, which can be viewed as the overlap between the fragment d_π orbital and the virtual orbital of CH_2S $3b_1(\pi^*)$. Therefore, we can conclude that the main bonding interaction in both systems is the π-back-donation from the transition metal to the unsaturated molecule. The strength of the π-back-donation can be related to the π* orbital energy of the CH_2X 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 CH_2X 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 0.1094 and 0.0433 au for free (undistorted) CH_2O and CH_2S, respectively, and decreases to 0.0677 au and −0.0019 au, respectively, upon distortion. The lower π* orbital energy of CH_2S is thus an indication that the π-back-donative interaction is more effective in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$ than in $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. This is in agreement with the measured ν(CO) bands of the adducts of $Os(CO)_2(PPh_3)_2$,[1] which also suggest that CH_2S is a stronger π-acceptor ligand than CH_2O.

The conclusion that the π-back-donation is the main channel of interaction between iron and the CH_2X molecules in the complexes investigated is also confirmed by the results of the Mulliken population analysis reported in Table III, which assigns a negative charge to the coordinated CH_2X species. The Mulliken population allows us to assign an oxidation state significantly different from the formal one, which foresees either +2 and −2 for iron and CH_2X, respectively, or zero for both. The results of Table III show that coordination of CH_2X implies a flow of electron density from the CO and PH_3 ligands toward iron and then to the unsaturated molecule. We note, however, that the net negative charge on CH_2S is computed to be appreciably smaller (by 0.35 electron) by use of basis II than by use of basis I, whereas the basis set change has a minor effect on the computed negative charge on coordinated CH_2O (0.17 electron decrease). This suggests the presence of a nonnegligible ligand-to-metal σ-donative contribution to the interaction between thioformaldehyde and iron, which is better described by basis II than by basis I and is almost absent in the case of CH_2O coordination. The π-orbital energy of CH_2S, shown in Table III, is about 0.1 au higher than that of CH_2O. This finding provides further evidence for the above conclusion. It seems clear that the σ-donative interaction should

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[42] Foster, J. M.; Boys, S. F. Rev. Mod. Phys. 1960, 32, 300.

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 two complexes (basis I), whereas the population is larger in the CH_2S complex (basis II).

Comparative Study of the Iron–Formaldehyde and Iron–Acetone Bonds. $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ show a bonding structure entirely comparable to the one described for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$. The molecular orbital analysis again shows that in both the iron–tetraphosphine formaldehyde and acetone complexes there is essentially one bonding orbital, i.e. the highest occupied molecular orbital (HOMO), which describes a π-back-donative interaction between the iron d_π orbital and the π^* orbital of formaldehyde and acetone. The fact that bonding is dominated by a net electron charge flow from the iron substrate to the unsaturated ligand is again confirmed by the net negative charge residing on the coordinated ligand (see Table III). From Table II we notice, however, that the formaldehyde adduct of iron–tetraphosphine is found to have a binding energy remarkably higher than that of $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$. This larger binding energy results from the nearly doubled iron–formaldehyde interaction energy, which overcompensates the increased deformation energy of CH_2O itself. As has previously been discussed,[17] an increase in interaction energy is to be expected upon replacement of carbonyl ligands with the stronger electron donor phosphine ligands, leading to an increased π-back-donative capability of the iron atom toward CH_2O. Indeed, the presence of electron-donor ligands, such as the phosphine, increases the electron density at the iron atom and hence the π-back-donation and the strength of the interaction between Fe and CH_2O. We see from Table III that the increase in Mulliken population (basis I) on formaldehyde upon coordination is 0.64 for $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$ and 0.83 for $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$. This increase of π-back-donation implies an increase of the strength of the iron–formaldehyde bond, as suggested by the interaction energy, which is −45.9 and −86.7 kcal·mol^{-1} for the iron–dicarbonyl–diphosphine and iron–tetraphosphine compounds, respectively (see Table II). The ligand influence can be explained in a different way by considering the energy of the fragment d_π orbital, which lies at −0.2657 au in $Fe(CO)_2(PH_3)_2$ and at −0.1647 au in $Fe(PH_3)_4$. The replacement of CO by PH_3, therefore, decreases the gap between the CH_2O π^* and the fragment d_π orbitals: hence, the overlap increases.

As shown in Table II, the acetone adduct of $Fe(PH_3)_4$ is computed to have a binding energy (−36.8 kcal·mol^{-1}) substantially smaller than that of the corresponding complex of CH_2O (−59.2 kcal·mol^{-1}). The difference in stability of the two complexes is understood by analyzing the deformation and interaction contributions to the binding energy. Once formaldehyde and acetone have undergone the geometry rearrangement required for coordination, they give rise to interactions with the iron substrate of entirely comparable strengths (the interaction energy for acetone is actually computed to be even higher than that for CH_2O). This result is in line with the comparable π^*-orbital energies of CH_2O and CMe_2O, which are computed to be 0.1094 and 0.1356 au, respectively, at the equilibrium geometries and 0.0507 and 0.0582 au, respectively, at the distorted geometries. We are thus led to the interesting conclusion that the lesser overall stability of the acetone complex can be entirely attributed to the higher deformation energy of CMe_2O, which is nearly twice that of CH_2O, rather than to a weaker acidity of the C═O unit.

Conclusions

The study of "ab initio" LCAO–MO–SCF level of the systems $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$ has shown that the main bonding interaction between the iron fragment and the unsaturated molecule is the π-back-donation from the transition metal to the π-acceptor ligand. 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. The deformation of the unsaturated molecule upon coordination is seen to be satisfactorily reproduced when comparison with experimental data is possible.

Bonding to iron is found to be stronger with thioformaldehyde than with formaldehyde. The reasons are that the former is a better π-acceptor ligand than the latter; furthermore, some nonnegligible contribution to the bonding comes from ligand-to-metal σ-donation.

The π-back-donation is comparable in $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$ and $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$. Nevertheless, the acetone molecule exhibits a weaker bond than formaldehyde since the destabilization energy required by the geometrical deformation of CMe_2O upon coordination is higher.

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Registry No. $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2O)$, 111113-06-5; $Fe(CO)_2(PH_3)_2(\eta^2\text{-}CH_2S)$, 111113-07-6; $Fe(PH_3)_4(\eta^2\text{-}CH_2O)$, 111113-08-7; $Fe(PH_3)_4(\eta^2\text{-}CMe_2O)$, 111113-09-8.

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Identification and Characterization of Lithium Polysulfides in Solution in Liquid Ammonia

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This study uses Raman spectroscopy and UV–visible spectrophotometry for the identification and the characterization of lithium polysulfides in liquid ammonia solutions. It is shown that S_6^{2-} is the least reduced polysulfide; S_6^{2-} is in equilibrium with the radical $S_3^{\bullet-}$. This equilibrium is strongly temperature dependent, and the equilibrium constant is 4.3×10^{-3} M at 293 K. A weak disproportionation of S_6^{2-} is shown, through the observation of S_4N^-. The existence of S_4^{2-} in solution is proved. This species was found to disproportionate as demonstrated by the observation of $S_3^{\bullet-}$. The equilibrium constant for the disproportionation of S_4^{2-} is about 10^{-6} M, estimated from the absorbance of $S_3^{\bullet-}$. The disulfide S_2^{2-} exists in solution and has low solubility. The possible existence of S_5^{2-} in solution is also discussed.

Introduction

The aim of the present work is to contribute to the identification and the characterization of the lithium polysulfides in liquid ammonia solutions. Bergstrom,[1] Zintl et al.,[2] Watt and Otto,[3] and Nelson[4] have already contributed to the identification of the alkali polysulfides in solution in liquid ammonia. Nelson[4] was

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(1) Bergstrom, F. W. *J. Am. Chem. Soc.* **1926**, *48*, 146.