

Study of Relative Stabilities of the Intermediates in Catalytic Carbon Monoxide Hydrogenation Reactions: *Ab initio* Calculations on the Model Compounds $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2\text{H}_2]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$, and $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$

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Ab initio calculations have been performed on the model compounds $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2\text{H}_2]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$, and $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$ to investigate the relative stabilities of the intermediates in catalytic carbon monoxide hydrogenation reactions. The results suggest that the formaldehyde compound can be obtained *via* insertion of CO into the Fe–H bond and subsequent rearrangement of the hydrido–formyl intermediate, in agreement with a proposed mechanism of the Fischer–Tropsch synthesis. Partial geometry optimizations obtained by gradient calculations show that the migration of one hydrogen of the co-ordinated formaldehyde in $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$ to iron to give $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$ is not allowed, while the migration of the same hydrogen to an adjacent CO to yield $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$ is energetically favoured.

The $\text{M}(\text{CH}_2\text{O})$ functionality plays a critical role in catalytic carbon monoxide reduction.^{1–5} Its various interrelated forms (see Scheme 1), their mode and energetics of conversion are crucial for understanding the different pathways leading to CO hydrogenation.

The only form which has been the subject of *ab initio* theoretical investigations is the formaldehyde complex.^{6,7} In this paper we analyse the relative stability of some species related to it, using the metallic fragment $\text{Fe}(\text{CO})_2(\text{PH}_3)_2$ because of its relationship with two compounds reported in the literature, $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\text{CH}_2\text{O})]$ and $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2\text{H}_2]$.⁸ In this work we have studied through *ab initio* Hartree–Fock calculations, the compounds $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2\text{H}_2]$, $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$, and $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$. The chemical reactions leading to interconversion of the forms studied here are shown in Scheme 2 and some of them, *i.e.* (a) and (b), have been reported.^{9–11} The choice of an iron substrate seems to be appropriate in view of the important role played by this metal as a catalyst in carbon monoxide hydrogenation reactions.^{1,3–5}

Computational Details

Basis Sets.—The two basis sets used in this work (denoted I and II) and details of the calculations are described in ref. 7. The geometry optimizations, described here, have been carried out using basis I, while subsequent single-point SCF (self consistent field) calculations at the optimized geometries were performed using the more extended basis II of double-zeta quality.

Ab initio spin-restricted Hartree–Fock SCF gradient calculations were used in partial geometry optimizations of the systems under investigation and in evaluating the energetics of the analysed reactions.

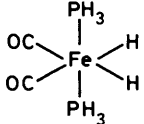
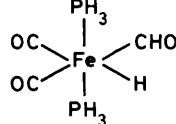
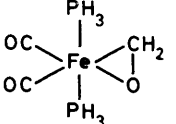
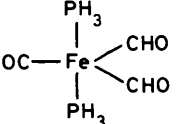
All computations were performed using the GAMESS program package¹² implemented on the cluster of ten FPS-

164 processors at the IBM European Center for Scientific and Engineering Computing (E.C.S.E.C., Rome).

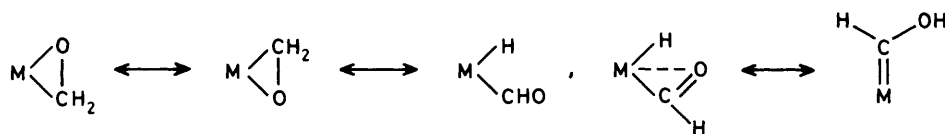
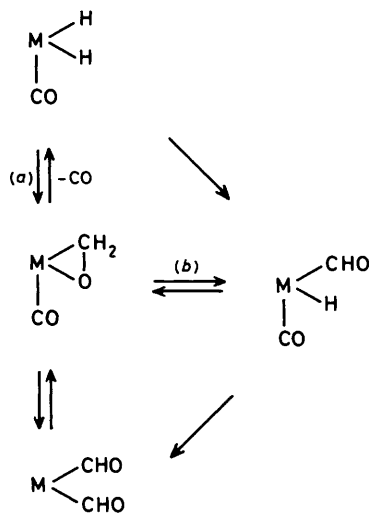
Geometries and Geometry Optimization.—In the partial geometry optimization calculations we optimized the geometrical parameters involving the iron atom and the atoms of the formaldehyde, formyl, and hydride ligands, with the formaldehyde side-on co-ordinated to the iron, in agreement with the structures of known transition-metal complexes involving CH_2O .^{8,9,13–17} The geometry of the $\text{Fe}(\text{CO})_2(\text{PH}_3)_2$ group in the systems $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2\text{H}_2]$, $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$, and $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$ was kept fixed at the values appropriate to the formaldehyde complex, as described in ref. 7, while that of the $\text{Fe}(\text{CO})(\text{PH}_3)_2$ fragment in $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$ was derived from the geometrical parameters of $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2]$ and kept fixed during the optimization. The experimental geometry has been used for free CO.¹⁸

The optimized structures of the complexes under investigation are shown in Table 1. A comparison with experimental data is possible only for $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CH}_2\text{O})]$, a model system for the well characterized compound $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\text{CH}_2\text{O})]$.⁸ The distortion of the formaldehyde molecule upon co-ordination 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 $[\text{Ni}(\text{PET}_3)_2(\text{CPh}_2\text{O})]$.¹⁹ The iron–formaldehyde bond is slightly asymmetric, with the Fe–C distance (2.03 Å) longer than Fe–O (2.00 Å). Our partially optimized structure satisfactorily reproduced 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 magnitude. The calculated C–Fe–O

Table 1. Partially optimized geometries of the systems under investigation; bond lengths in Å, angles in °

							
Fe-H	1.566	Fe-C	2.044	Fe-C	1.952 (2.03) ^a	Fe-C	2.078
H-Fe-CO	75.4	Fe-H	1.726	Fe-O	1.971 (2.00) ^a	C-O	1.248
		C-O	1.240	C-O	1.311 (1.32) ^a	C-H	1.110
		C-H	1.116	C-H	1.082	C-Fe-CO	93.6
		C-Fe-CO	96.7	C-Fe-CO	102.1 (108.5) ^a	H-C-Fe	125.6
		H-C-Fe	129.0	H-C-H	112.4	O-C-Fe	120.6
		O-C-Fe	116.9	α^b	29.1		
		C-Fe-H	112.5				

^a Experimental values relative to $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OMe})_3\}_2(\text{CH}_2\text{O})]$. ^b α is the distortion angle defined as the angle between the CH_2 plane and the C-O bond.

**Scheme 1.****Scheme 2.**

angle of 39.0° , obtainable from the values in Table 1, is in excellent agreement with the experimental estimate of 38.2° .

The metallic fragment we used allows η^2 -co-ordination for CH_2O and σ -co-ordination for the formyl group: the H-C-Fe angle, indeed, is calculated to be 129.0° in $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$ [125.6° in $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$], a value very close to that calculated by Hoffmann and co-workers²⁰ for $[\text{Mn}(\text{CO})_5(\text{COMe})]$ (C-C-Mn, 128°). The Fe-C distance in $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$ is computed to be 2.044 \AA [2.078 \AA in $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$] and is slightly longer than the Fe-C distance of 1.97 \AA in the benzoyl complex $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{COPh})(\text{CO})(\text{PPh}_3)]$ ²¹ and 1.968 \AA in the acetyl complex $[\text{Fe}\{\text{HB}(\text{pz})_3\}(\text{COMe})(\text{CO})_2]$ [$\text{HB}(\text{pz})_3$ = hydrotris(pyrazol-1-yl)borate],²² but is shorter than the alkyl Fe-C distance of 2.11 \AA found in $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\eta^3\text{-C}_3\text{H}_5)(\text{CO})(\text{PPh}_3)]$.²³ This shortening of the formyl bond is generally explained by

invoking metal-to-formyl back-donation. The C-O bond length of 1.24 \AA calculated for $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$ [1.248 \AA for $[\text{Fe}(\text{CO})(\text{PH}_3)_2(\text{CHO})_2]$] compares well with that found in $[\text{Fe}(\eta\text{-C}_5\text{H}_5)(\text{COPh})(\text{CO})(\text{PPh}_3)]$ (1.22 \AA)²¹ and is clearly shorter than that typical of a C-O single bond ($1.41\text{--}1.43 \text{ \AA}$).²⁴ Finally the Fe-H distance of 1.726 \AA , longer than that calculated for $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2\text{H}_2]$ (1.566 \AA), suggests that this bond in $[\text{Fe}(\text{CO})_2(\text{PH}_3)_2(\text{CHO})\text{H}]$ is weakened.

Discussion

Optimized geometries reported in Table 1 show that the formyl group is σ bonded. This is in agreement with the experimental structure of all the iron-formyl and -acyl compounds so far reported²⁵ for saturated iron complexes. Early transition metals as well as actinides prefer η^2 -co-ordination^{20,25-27} because of the oxophilicity of the metal and its unsaturation. This problem has been satisfactorily explained by Hoffmann and co-workers;²⁰ overlap reasons lead to η^2 -co-ordination in the complexes of metals with less than six d electrons, while for metals having a d^6 electronic configuration or more the η^2 -mode gives rise to a repulsive interaction between occupied orbitals.

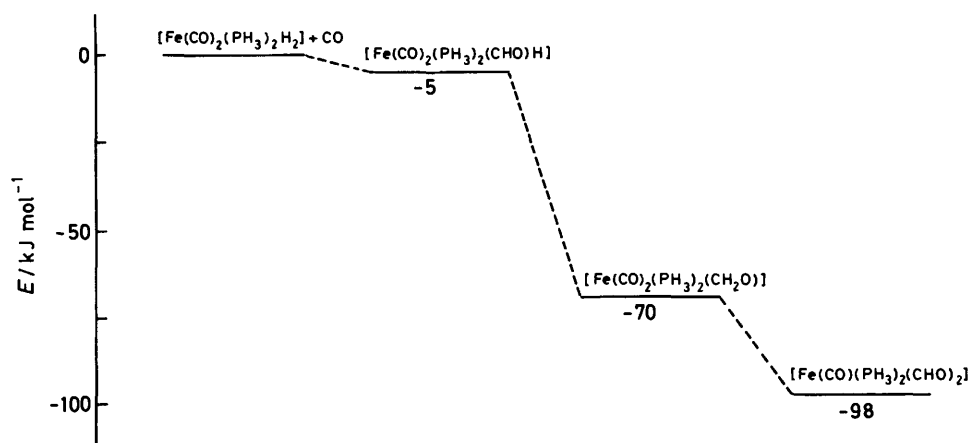
The analysis of the molecular orbitals of the compounds with the formyl group shows that the iron orbitals which participate in the bonding are hybrid orbitals which strongly involve the Fe $4s4p$ shell. Indeed there is a consistent occupation of this shell as suggested by the results of the Mulliken analysis reported in Table 2, which assigns a population greater than 0.4 and 0.6 electrons to the $4s$ and $4p$ orbitals, respectively.

The co-ordination bonding mode of the formaldehyde molecule has been discussed elsewhere;⁷ the main bonding interaction between the iron and the formaldehyde is the π back-donation from an occupied orbital of the metal to a virtual orbital of the ligand. The C-O bond in the formaldehyde molecule is lengthened upon co-ordination, as is suggested by the overlap population which is only 0.29 electrons (see Table 2). The C-O bond in the formyl group is undoubtedly stronger, exhibiting a higher overlap population ($0.51\text{--}0.52$ electrons)

Table 2. Mulliken population analysis of the systems under investigation

Fe $\left\{ \begin{array}{l} s \\ p \\ d \end{array} \right.$	6.48 12.68 7.14	6.40 12.68 7.06	6.35 12.65 7.17	6.44 12.65 6.86
Axial ligands (PH ₃)	35.53	35.40	35.48	35.39
Equatorial ligands (CO)	27.84	27.98	27.88	13.80
L*	2.33	16.48	16.47	30.86
Overlap populations				
	FeH 0.28	FeC ¹ 0.28 FeH 0.10 C ¹ H 0.26 C ¹ O 0.51	FeC ¹ 0.10 FeO 0.11 C ¹ H 0.36 C ¹ O 0.29	FeC ¹ 0.29 C ¹ H 0.25 C ¹ O 0.52
	FeC 0.10	FeC ² 0.08 FeC ³ 0.18	FeC ² 0.15 FeC ³ 0.09	FeC ² 0.12
	FeP 0.12	FeP 0.17	FeP 0.14	FeP 0.16

* L is the hydrido, hydrido-formyl, formaldehyde, or diformyl ligands.

**Figure.** Relative energies of the analysed systems

and a shorter distance (1.240 Å compared to 1.311 Å in the CH₂O compound). The overlap populations of Table 2 suggest that the Fe–H bond in [Fe(CO)₂(PH₃)₂H₂] is stronger than that in [Fe(CO)₂(PH₃)₂(CHO)H], as already noted on the basis of the optimized structures. From Table 2 we can also notice a slight decrease in the iron *d* population on going from the compound with CH₂O to those with CHO.

The Figure reports the relative energies of the analysed systems. The formyl compound [Fe(CO)₂(PH₃)₂(CHO)H] is computed to be stable towards dissociation into [Fe(CO)₂(PH₃)₂H₂] and CO by only 5 kJ mol⁻¹. This very small value does not allow a definitive statement to be made concerning the stability of [Fe(CO)₂(PH₃)₂(CHO)H], since correlation effects are not included in our calculation. The energy lowering is substantially greater (65 kJ mol⁻¹) when [Fe(CO)₂(PH₃)₂(CHO)H] is converted into [Fe(CO)₂(PH₃)₂(CH₂O)], which, however, is computed to be less stable by 28 kJ mol⁻¹ than [Fe(CO)(PH₃)₂(CHO)₂].

Our calculations suggest that the insertion of CO into an Fe–H bond implies a very slight energy change. It is generally believed²⁵ that CO migration into a metal–hydrogen bond is an endothermic reaction while insertion of CO into a metal–alkyl bond is exothermic and this difference lies in the fact that metal–

hydrogen bonds are stronger than metal–carbon bonds by up to 120 kJ mol⁻¹.^{27,28}

A few examples, however, have been reported confirming a formal insertion of CO into an M–H bond: [Rh(oep)H] leads to [Rh(oep)(CHO)] (oep = 2,3,7,8,12,13,17,18-octaethylporphyrin)²⁹ and the reaction of carbon monoxide with oxophilic metal–hydrido complexes containing Th and Zr.^{10,11,27} The driving force in the latter cases is the oxophilicity of the metal. This feature should play a less important role in our model complexes, as well as for the metals used in Fischer–Tropsch synthesis. Even in the absence of this additional driving force our calculations show that the carbonylation of a metal–hydride may well be expected to be possible.

The rearrangement of a metal–hydrido–formyl complex into a formaldehyde complex [see path (b) in Scheme 2] is a pathway which may be relevant in CO hydrogenation. In the iron system under analysis, the lowering in energy upon rearrangement of the hydrido–formyl group into a formaldehyde ligand is calculated to be 65 kJ mol⁻¹. Such a reaction has been proposed to lead to the formation of [ZrCl(η-C₅H₅)₂](CH₂O)],¹⁰ while the inverse one has been reported for the compound [Os(CO)₂(PPh₃)₂(CH₂O)].⁹ The formaldehyde complex has not even been observed in the oxidative addition of CH₂O to

several iridium(I) complexes.³⁰ Our calculations indicate that the migration of one hydrogen from CH₂O to the iron in [Fe(CO)₂(PH₃)₂(CH₂O)] is energetically disfavoured, while its migration to an adjacent CO to yield two formyl ligands is exothermic by 28 kJ mol⁻¹. This may be a relevant pathway in the hydrogenation of CO, although it has never been observed in stoichiometric reactions. Examples of formyl complexes with two formyl ligands have been reported²⁵ and their presence as intermediates has been supposed in the mechanism of the homogeneous hydrogenation of carbon monoxide.² The latter mechanism would generally imply the rearrangement of a diformyl complex into a formaldehyde-carbonyl one. Our calculations suggest that in the case of an iron substrate the reverse reaction should take place.

Acknowledgements

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