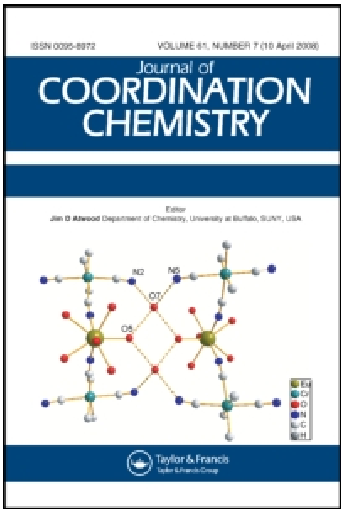
This article was downloaded by:
On: *23 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THEORETICAL COMPARISON OF THE BONDING OF CHALCOCARBONYL LIGANDS

Ted A. O'Brien[a]; James F. O'Brien[a]
[a] Department of Chemistry, Southwest Missouri State University, Springfield, MO

To cite this Article O'Brien, Ted A. and O'Brien, James F.(1998) 'THEORETICAL COMPARISON OF THE BONDING OF CHALCOCARBONYL LIGANDS', Journal of Coordination Chemistry, 44: 1, 91 — 99
To link to this Article: DOI: 10.1080/00958979808022883
URL: http://dx.doi.org/10.1080/00958979808022883

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Coord. Chem., 1998, Vol. 44, pp. 91–99
Reprints available directly from the publisher
Photocopying permitted by license only

© 1998 OPA (Overseas Publishers Association)
N.V. Published by license under
the Gordon and Breach Science Publishers imprint
Printed in Malaysia

THEORETICAL COMPARISON OF THE BONDING OF CHALCOCARBONYL LIGANDS

TED A. O'BRIEN and JAMES F. O'BRIEN*

[a]*Department of Chemistry, Southwest Missouri State University, Springfield, MO 65804*

(Received 14 February 1997; Revised 12 May 1997; In final form 18 September 1997)

Downloaded At: 15:23 23 January 2011

Fenske-Hall molecular orbital calculations on the complexes $CpFe(CO)_2(CX)^+$ (X = O, S, Se, and Te) have been used to quantify the nature of bonding between the CX ligands and the metal atom. In addition, conclusions have been reached about the reactivity of the complexes under both nucleophilic and electrophilic attack. The previously established trend of increasing metal—ligand bond strength as X changes from O to S to Se is demonstrated by our molecular orbital calculations, and found to extend to Te. The mechanism for nucleophilic attack, variously explained in the past by either charge control or orbital control, is quantitatively ascribed to orbital control only. The nature of electrophilic attack on these complexes is also found to begin with orbital control.

Keywords: carbon monoxide; carbon monosulfide; carbon monoselenide; carbon monotelluride; molecular orbital calculation

INTRODUCTION

It is widely accepted that CS bonds more strongly to metal atoms in complexes than does CO.[1-7] Replacement reactions involving complexes containing both CO and CS as ligands generally result in replacement of the CO and retention of the CS.[2-7] In addition, molecular orbital calculations revealed that CS interacts better with iron orbitals than does CO.[4,8] Both IR and NMR spectral data usually indicate stronger metal CX bonds for CS rather than CO.[9] Some have questioned the capability of IR data to distinguish σ and π contributions to bonding effects.[10-12] Thus the preferential replacement of CO has been attributed to stronger bond formation between the metal and CS than between the metal and

---

[*] Corresponding author.

CO. This study examines the bonding of CSe and CTe as ligands, and quantifies the relative strength of the interaction between the Fe atom and the entire family of CX ligands in the complexes $CpFe(CO)_2(CX)^+$.

Reaction of nucleophiles with such complexes generally results in attack of the nucleophile at the carbon atom of CS and not at the carbon atom of CO.[6-8,13,14] Some have attributed this to charge control of the mechanism,[7,15] while others have invoked orbital control of the reaction.[8] The results of our Fenske-Hall molecular orbital calculations reveal that the relative charges on the CX ligands change in a manner exactly opposite to that required to explain relative tendencies for nucleophilic attack. On the other hand, the nature of the LUMO varies in the CX molecules in precisely the proper way to explain the relative tendencies for reaction with nucleophiles.

Reactions of electrophiles with complexes containing CO and/or CS ligands generally result in attack of the electrophile at the X atom of the CX ligand.[1,6,13] Once again our calculations suggest orbital control of the reaction.

Downloaded At: 15:23 23 January 2011

EXPERIMENTAL

Fenske-Hall molecular orbital calculations were done on an IBM 4381 mainframe computer. The Fenske-Hall method assumes a fixed molecular structure.[16,17] The X-ray structure of the parent compound, $CpFe(CO)_3^+$, was taken from the literature.[18] It was then modified for the $CpFe(CO)_2(CX)^+$ complexes by placing the X atoms at distances appropriate for their covalent radii relative to that of oxygen. The atomic basis functions used were those of Herman and Skilman[19] as modified with the $X\alpha$ to Slater basis program of Bursten and Fenske.[20,21] A Mulliken population analysis was used to determine the atomic orbital occupancies and the atomic charges. Whenever appropriate fragment basis calculations were performed. In these fragment calculations, as discussed in detail by Housecroft and Fehlner,[22,23] the molecular orbitals for each group of interest, in their proper spatial positions, are first calculated. Then these fragments are combined with the rest of the complex to form the final species whose molecular orbitals are then calculated.

RESULTS AND DISCUSSION

Extent of Interaction Between CX and the $CpFe(CO)_2^+$ Fragment

Use of the fragment basis approach in the Fenske-Hall molecular orbital calculations clearly shows the number of electrons in CX molecular orbitals both

TABLE I Electron transfer between Fe and CX

Compound	*Ligand*	σ_{HOMO}	σ_{inner}	σ_{tot}	π_{don}	*Total*
$CpFe(CO)_3^+$	CO	0.65	0.02	0.67	0.46	1.13
$CpFe(CO)_2(CS)^+$	CO	0.59	0.04	0.63	0.46	1.09
	CS	0.64	0.06	0.70	0.49	1.19
$CpFe(CO)_2(CSe)^+$	CO	0.64	0.02	0.66	0.45	1.11
	CSe	0.63	0.08	0.71	0.56	1.27
$CpFe(CO)_2(CTe)^+$	CO	0.63	0.02	0.65	0.45	1.10
	CTe	0.61	0.12	0.73	0.58	1.31

before and after complexation to the remainder of the $CpFe(CO)_2(CX)^+$ ion. In all cases the free CX molecules have two electrons in the CX σ type orbital that closely corresponds to the lone pair on the C atom; there are zero electrons in the LUMO, which consists of the doubly degenerate anti-bonding π^* molecular orbitals. Following complex formation the number of electrons in these CX orbitals varies. Thus the fragment basis calculation allows one to clearly see the amount of electron density donated by CX to the Fe atom in σ type orbitals and accepted by CX from the Fe atom into its π^* orbitals.

In addition to these rather standard interactions involving the highest occupied σ orbital and the lowest unoccupied π orbital of the CX molecules, there occurs in these complexes a third mode of interaction. The CX molecules also donate a small amount of electron density to the Fe atom from an inner σ type bonding orbital. We also find evidence of some interaction of the π bonding orbital of CX with the $CpFe(CO)_2^+$ fragment, as others have noted.[8,24] However, this interaction does not result in a transfer of electrons from CX to the $CpFe(CO)_2^+$ fragment. The π bonding orbitals of CX each have two electrons both before and after complex formation. The combination of the three effects results in a total transfer of electrons, shown in Table I, that increases from an average of 1.11 for CO to 1.31 for CTe. The number of electrons transferred is a measure of the amount of bonding. Thus the sum of the number of electrons transferred in the σ and π modes is a measure of the total amount of bonding between the metal and the CX ligand. This same approach has been previously used as a measure of bond strength.[25] It suggests that the trend of increasing interaction between CX and Fe, previously reported for CO, CS, and CSe,[26] continues on, not unexpectedly, to CTe. Table I shows that the CTe molecule is both the best σ bonder and the best π bonder to the Fe atom.

Factors which might play a role in determining the number of electrons transferred to and from the ligand are the electronic charges on the atomic centers accepting or donating the electrons and the relative energies of the ligand orbitals accepting or donating the electrons. Table II contains the charges on the carbon

Downloaded At: 15:23 23 January 2011

TABLE II Results of Fenske-Hall calculations on free CX molecules

	Q_C	*Percentage of atomic orbitals in free CX*		
			HOMO	*LUMO*
CO	−0.094	C	78	67
		O	22	33
CS	−0.388	C	71	63
		S	29	37
CSe	−0.412	C	68	63
		Se	32	37
CTe	−0.478	C	65	63
		Te	35	37

Downloaded At: 15:23 23 January 2011

atoms of the free CX molecules. The carbon atom of CX gets more negative as one proceeds from CO (Q_C=−0.094) to CTe (Q_C=−0.478). The large negative charge on its carbon atom means that CTe approaches the Fe atom with the greatest tendency to repel electrons. This would tend to make CTe the best σ donor and the worst π acceptor. Thus, while the charges on the carbon atoms are compatible with the σ donation trend, they cannot explain the trend in π acceptance. For transfer of π electrons the observed result is exactly opposite to that predicted by carbon atom charges. It is conceivable that the charge accepted by CX molecules upon bonding to the Fe atom could end up on the X atom. Note that if the π^* LUMO in the free CX molecules were centered on the X atom in CX, then the accepted electrons would end up mainly on the X atom and not on the carbon atom. From a charge standpoint this would be favorable since the sulfur, selenium, and tellurium atoms in free CX molecules are all positively charged. However, in Table II we present the carbon atom and X atom orbital percentages that make up the LUMO in the four free CX molecules. As can be seen, in all four CX molecules the LUMO is mainly centered on the carbon atom.

We must look elsewhere for an explanation of the number of π electrons transferred from the iron atom to the carbon atom of CX. The other possible factor affecting the amount of electron density transferred is the energy match between the donor and acceptor orbitals in the interaction. The energy values are given for both the σ and the π interactions in Table III. Values from this table have been plotted in Figure 1. The energy match between the orbitals of the $CpFe(CO)_2^+$ fragment and the orbitals of CX is best for CTe and worst for CO in the case of both σ and π bond formation.

Note that the orbital energy match for σ interaction, given in Table III and graphed in Figure 1, can also explain the trend in σ electron donation. The CO σ orbital energy match is the worst; the CTe σ orbital energy match is the best. Thus both charge and orbital considerations favor the observed superior σ

TABLE III Computed energies of donor and acceptor orbitals

Compound	*Orbital Energy*				
	σ acceptor	*σ donor*	*π donor*	*π acceptor*	
	Fe	*CX*	*Fe*	*CO*	*CX*
$CpFe(CO)_3^+$	−12.6 eV	−20.3 eV			
$CpFe(CO)_2(CS)^+$	−12.6	−17.2	−15.8 eV	−6.3	−8.2
$CpFe(CO)_2(CSe)^+$	−12.6	−16.2	−15.8	−6.3	−9.6
$CpFe(CO)_2(CTe)^+$	−12.6	−15.2	−15.8	−6.1	−9.9
	CO CS CSe CTe			CO CS CSe CTe	
	ΔE_σ 7.7 4.6 3.6 2.6			ΔE_π 9.6 7.6 6.2 5.9	

interaction of CTe with the metal containing fragment, $CpFe(CO)_2^+$. As noted above, we find that a small amount of electron density is transferred out of a lower level σ bonding CX orbital (4σ in CO for example).

The good energy match between the metal-containing fragment and the π* LUMO of CTe, see Figure 1, provides the driving force for the larger transfer of π electrons in that complex. Table III shows that the energy of the π acceptor orbital in CTe is closest to the energy of the donor orbital of the metal-containing fragment. The π-orbital on CO has the worst energy match with the metal fragment.

Thus our results extend the reported trend to CSe and CTe, and suggest the amount of electron transfer depends more on the relative energies of donor and acceptor orbitals and less on the atomic charges; CTe is the best π electron acceptor because of orbital effects and in spite of charge effects.

Site of Nucleophilic and Electrophilic Attack

It is known that the site of nucleophilic attack in complexes containing both CO and CS is normally at the carbon atom of CS.[6-8,13] Table IV shows the computed charges on atoms in the complexes. The charge on the carbon atom of CX gets more negative as one proceeds down the periodic chart, maximizing at the −0.415 charge on the carbon atom of CTe. Despite the negative charge on the carbon atom of CS and the positive charge on the carbon atom of CO, the site of nucleophilic attack in the complex is the carbon atom of CS. The negative charge on this carbon atom strongly suggests that nucleophiles attack there because of orbital considerations. Table V shows the percentages of atomic and fragment orbitals in the π* LUMO of the $CpFe(CO)_2(CX)^+$ complexes. These data can be used to evaluate an orbital explanation of the site of nucleophilic attack. Under orbital control attack will occur at the atom that makes the greatest contribution to the LUMO. That will permit the pair of electrons being donated by the

Downloaded At: 15:23 23 January 2011

Downloaded At: 15:23 23 January 2011

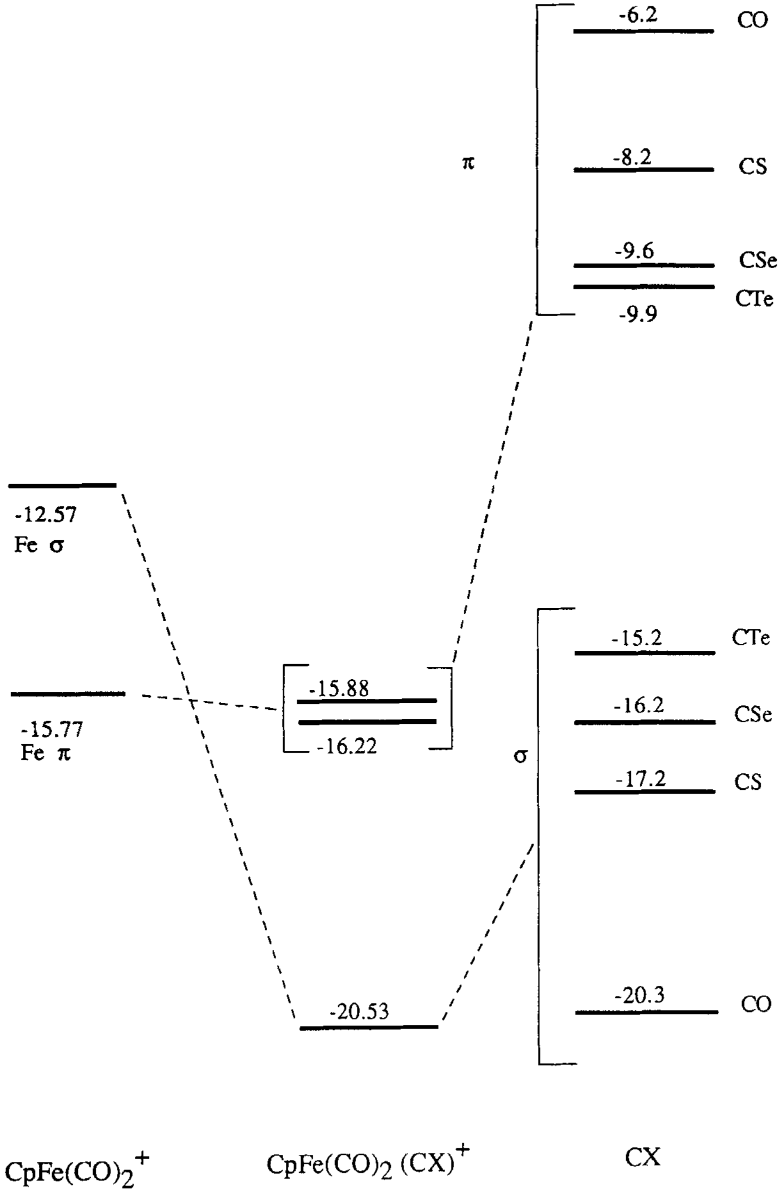


FIGURE 1 Molecular orbital diagram for $CpFe(CO)_2(CX)^+$

TABLE IV Atomic charges in $CpFe(CO)_2(CX)^+$ complexes

Compound	*Atom*	*Q*
$CpFe(CO)_3^+$	Fe	+0.429
	*C*O	+0.136
	C*O*	+0.057
$CpFe(CO)_2(CS)^+$	Fe	+0.508
	*C*O	+0.132
	C*O*	+0.048
	*C*S	−0.237
	C*S*	+0.422
$CpFe(CO)_2(CSe)^+$	Fe	+0.535
	*C*O	+0.138
	C*O*	+0.047
	*C*Se	−0.318
	C*Se*	+0.463
$CpFe(CO)_2(CTe)^+$	Fe	+0.559
	*C*O	+0.138
	C*O*	+0.042
	*C*Te	−0.415
	CTe	+0.563

TABLE V Composition of the HOMO and LUMO in $CpFe(CO)_2(CX)^+$ complexes

Compound	*Site*	*Atomic Orbital*	*LUMO Percentage*	*HOMO Percentage*
$CpFe(CO)_3^+$	C	s, p	10	3
	O	s, p	5	7
	Fe	3d	33	59
$CpFe(CO)_2(CS)^+$	*C*O	s, p	1	2
	C*O*	s, p	1	2
	Fe	3d	20	55
	*C*S	s, p	39	1
	C*S*	s, p	27	20
$CpFe(CO)_2(CSe)^+$	*C*O	s, p	0	2
	C*O*	s, p	0	2
	Fe	3d	12	46
	*C*Se	s, p	49	0
	C*Se*	s, p	34	34
$CpFe(CO)_2(CTe)^+$	*C*O	s, p	0	1
	C*O*	s, p	0	1
	Fe	3d	12	36
	*C*Te	s, p	9	3
	CTe	s, p	36	

Downloaded At: 15:23 23 January 2011

nucleophile to find the lowest available energy site. As shown in Table V, whenever CS, CSe, or CTe is present, the contribution of CO to the LUMO is essentially zero. In $CpFe(CO)_2(CS)^+$ and $CpFe(CO)_2(CSe)^+$ the LUMO is mainly present on the carbon atom of CS and CSe. Orbital control correctly predicts nucleophilic attack at these sites. Charge control does not.

The $CpFe(CO)_2(CTe)^+$ complex is very interesting. Not only is the charge distribution different than the other complexes, but the orbital makeup of the LUMO is also different. Table IV shows that charge control of nucleophilic attack would lead to reaction at the tellurium atom. The composition of the LUMO of the $CpFe(CO)_2(CTe)^+$ complex, given in Table V, indicates that orbital control would also lead to nucleophilic attack at the tellurium atom not at a carbon atom. Experimental testing of this prediction will aid future theoretical studies.

Electrophilic attack on the $CpFe(CO)_2(CX)^+$ complexes normally occurs at the X atom.[1,6,13] The data in Table IV indicate that charge control of the reaction incorrectly predicts electrophilic attack at the carbon atoms of CX except when X = O. In $CpFe(CO)_3^+$ the only negatively charged sites are on the Cp ring. The charge on the X atom gets more positive as one moves down the periodic chart. The maximum value is found to be +0.563 on Te. The site of greatest positive charge is the sterically hindered metal atom. When CO is present with another CX ligand, the carbon atom of CO is always more positive than the carbon atom of CX. For example in $CpFe(CO)_2(CS)^+$ the carbon atom of CO has a charge of +0.132 compared with the carbon atom of CS having a charge of −0.237. Again one needs to look at orbital considerations in order to explain the observed electrophilic attack at X atoms. Table V gives the composition of the carbon atom lone pair orbitals, usually the HOMO, in the $CpFe(CO)_2(CX)^+$ complexes. Under orbital control electrophilic attack would occur at that atom which predominates in the HOMO. When $X \neq O$ there is always a large contribution in the HOMO from the X atom. Thus in these complexes the site of electrophilic attack is readily explained by orbital control of the mechanism. Again we find that $CpFe(CO)_2(CTe)^+$ is unique in that it is the only complex whose HOMO has a larger contribution from the X atom than from the iron atom. In summary, the known trend in strength of bonding of CX ligands to Fe is supported by the Fenske-Hall molecular calculations, and extended to CTe. The calculations also suggest that the site of both nucleophilic and electrophilic attack is due to orbital control of the mechanism. Charge control is most likely not operative.

Downloaded At: 15:23 23 January 2011

References

1. H. Werner, *Angew. Chem. Int. Edn. (Engl)*, **29**, 1077 (1990).
2. I.S. Butler, *Acc. Chem. Res.*, **10**, 359 (1977).

3. I.S. Butler and A.E. Fenster, *J. Organomet. Chem.*, **66**, 161 (1974).
4. J.W. Richardson Jr, R.J. Angelici, and R.A. Jacobson, *Inorg. Chem.*, **26**, 452 (1987).
5. I.S. Butler and J.F. Harrod, *Inorganic Chemistry*, Benjamin Cummins Publishing Company, Inc., Redwood City, CA, 1989.
6. P.V. Broadhurst, *Polyhedron*, **4**, 1801 (1985).
7. L. Bussetto and A. Palazzi, *Inorg. Chim. Acta*, **19**, 233 (1976).
8. D. Lichtenberger and R.F. Fenske, *Inorg. Chem.*, **15**, 2015 (1976).
9. H. Herberhold and P.D. Smith, *Angew. Chem., Int Edn. (Engl)*, **18**, 631 (1979).
10. R.J. Angelici and M.D. Malone, *Inorg. Chem.*, **6**, 1731 (1967).
11. L. Bussetto and R.J. Angelici, *J. Amer. Chem. Soc.*, **90**, 3283 (1968).
12. W.A.G. Graham, *Inorg. Chem.*, **7**, 315 (1968).
13. F.P. Pruchnik, *Organometallic Chemistry of the Transition Elements*, Plenum Press, N.Y., (1990).
14. W.W. Greaves, R.J. Angelici, B.J. Helland, R. Klima, and R.A. Jacobson, *J. Amer. Chem. Soc.*, **101**, 7618 (1979).
15. D.J. Darensbourg and M.Y. Darensbourg, *Inorg. Chem.*, **9**, 1691 (1970).
16. R.F. Fenske, *Pure and Applied Chem.*, **27**, 61 (1971).
17. M.B. Hall and R.F. Fenske, *Inorg. Chem.*, **11**, 768 (1972).
18. M.E. Gress and R.A. Jacobson, *Inorg. Chem.*, **12**, 1746 (1973).
19. F. Herman and S. Skillman, *Atomic Structure Calculations*, Prentice-Hall, Englewood Cliffs, N.J., (1963).
20. B.E. Bursten and R.F. Fenske, *J. Chem. Phys.*, **67**, 3138 (1977).
21. B.E. Bursten, R.J. Jensen, and R.F. Fenske, *J. Chem. Phys.*, **68**, 3320 (1978).
22. C.E. Housecroft and T.P. Fehlner, *Organometallics*, **2**, 690 (1983).
23. T.P. Fehlner and C.E. Housecroft, *Organometallics*, **3**, 764 (1984).
24. M.A. Andrews, *Inorg. Chem.*, **16**, 496 (1977).
25. R.G. Pearson, *Inorg. Chem.*, **23**, 4675 (1984).
26. J.Y. Saillard, D. Grandjean, P. Caillet and A. LE Baize, *J. Organomet. Chem.*, **190**, 371 (1980).

Downloaded At: 15:23 23 January 2011