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Transition-Metal Thiocarbonyls and Selenocarbonyls

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Since the end of the nineteenth century carbon monoxide has been known to bond to transition metals in low oxidation states to form metal carbonyls.¹ However, similar molecules containing the isoelectronic CS and CSe ligands have only been discovered in the past 10 years. One of the chief reasons for the relatively late development of the chemistry of transition-metal thio- and selenocarbonyls is undoubtedly the instability of CS and CSe compared to CO. Carbon monosulfide is a well-characterized species in the upper atmosphere² and has been shown to be intermediate in the photolysis and combustion of CS₂.³ It can be produced in gram quantities in the laboratory by passing a high-voltage ac discharge through CS₂ in a vacuum flow system.⁴ However, above -160 °C, a black-brown CS polymer is formed, and the polymerization often occurs explosively. Despite this difficulty, numerous spectroscopic studies have been carried out on the CS monomer.⁵ Carbon monoselenide appears to be even more unstable since it has thus far eluded isolation,⁶ although its electronic spectrum has been recorded.⁷

It is evident that CS can be stabilized by coordination to many transition metals, and well over 100 thiocarbonyl complexes have been reported, encompassing all the group 6B, 7B, and 8 metals, with the exception of technetium and palladium.⁸ Metal selenocarbonyls are still extremely rare and are at present restricted to complexes of chromium, manganese, rhenium,¹⁰ and ruthenium.¹¹ While the vast majority of metal thiocarbonyls and all the known metal selenocarbonyls contain terminal CX (X = S, Se) ligands, there are a few examples of thiocarbonyls with thioketonic and end-to-end CS bridging groups. X-ray studies have established that the bonding of the terminal CX^{11,12} and thioketonic ligands¹³ is similar to that in analogous metal carbonyls, i.e., coordination through carbon and, in the case of the terminal CX groups, linear metal-C-X linkages.

Owing to the isoelectronic nature of CO, CS, and CSe, there has been considerable interest in the comparative bonding properties of these three ligands. Molecular orbital calculations and PES measurements on CS itself

and on several metal thiocarbonyl complexes have indicated that CS is a better σ -donor and π -acceptor ligand than CO.¹⁴ The molecular orbitals for CO and CS are compared in Figure 1. The 7σ donor orbital of CS is at higher energy than the 5σ donor orbital of CO, while the 3π (π^*) acceptor level of CS is at lower energy than the 2π (π^*) acceptor level of CO. It should also be mentioned that the 7σ level of CS is significantly antibonding in character. At the present time there are no molecular orbital data available for CSe or any metal selenocarbonyl complex. However, ¹³C NMR measurements on several series of group 6B and group 7B chalcocarbonyl complexes indicate that CSe is a better electron-withdrawing (σ -donor vs. π -acceptor) ligand than CS.^{15,16} The above results lead one to expect that metal-CX bonds should be appreciably stronger than metal-CO bonds in view of the synergistic interaction believed to be operative for this type of ligand.^{17,18}

The objectives of this Account are (1) to illustrate the currently available synthetic routes to metal thio- and

(1) L. Mond, C. Langer, and F. Quinke, *J. Chem. Soc.*, 57, 749 (1890); L. Mond and C. Langer, *J. Chem. Soc.*, 59, 1090 (1891).

(2) P. Harteck and R. Reeves, *Bull. Soc. Chim. Belg.*, 71, 682 (1962); D. Buhl, *Sky Telescope*, 156 (March 1973).

(3) For example, see W. P. Wood and J. Heicklen, *J. Phys. Chem.*, 75, 854, 861 (1971); M. DeDorgo, A. J. Yarwood, O. P. Strauz, and H. E. Gunning, *Can. J. Chem.*, 43, 1886 (1965).

(4) K. J. Klabunde, C. M. White, and H. F. Efner, *Inorg. Chem.*, 13, 1778 (1974).

(5) For example, see S. Silvers, T. Bergeman, and W. Klemperer, *J. Chem. Phys.*, 52, 4385 (1970); R. Steudel, *Z. Anorg. Allg. Chem.*, 364, 180 (1968).

(6) R. Steudel, *Angew. Chem., Int. Ed. Engl.*, 6, 635 (1967).

(7) R. K. Laird and B. F. Barrow, *Proc. Phys. Soc., London, Sect. A*, 66, 836 (1953).

(8) For a review on the chemistry of transition-metal thiocarbonyls up to March 1973, see I. S. Butler and A. E. Fenster, *J. Organomet. Chem.*, 66, 161 (1974). Most of the more recent references are cited in ref. 9.

(9) G. G. Barna, I. S. Butler, and K. R. Plowman, *Can. J. Chem.*, 54, 110 (1976).

(10) I. S. Butler, D. Cozak, and S. R. Stobart, *J. Chem. Soc., Chem. Commun.*, 103 (1975); *Inorg. Chem.*, 16, 1779 (1977).

(11) G. R. Clark, K. R. Grundy, R. O. Harris, S. M. James, and W. R. Roper, *J. Organometal. Chem.*, 90, C37 (1975).

(12) S. S. Woodward, R. A. Jacobson, and R. J. Angelici, *J. Organometal. Chem.*, 117, C75 (1976), and references therein.

(13) J. W. Dunker, J. S. Finer, J. Clardy, and R. J. Angelici, *J. Organomet. Chem.*, 114, C49 (1976).

(14) D. L. Lichtenberger and R. F. Fenske, *Inorg. Chem.*, 15, 2015 (1976), and references therein.

(15) D. Cozak and I. S. Butler, *Spectrosc. Lett.*, 9, 673 (1976).

(16) D. Cozak, Ph.D. Thesis, McGill University, Montreal, Quebec, Canada, 1977.

(17) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd ed, Wiley-Interscience, New York, N.Y., 1974.

(18) For a brief review of the bonding in octahedral metal carbonyls, see G. R. Dobson, *Acc. Chem. Res.*, 9, 300 (1976).

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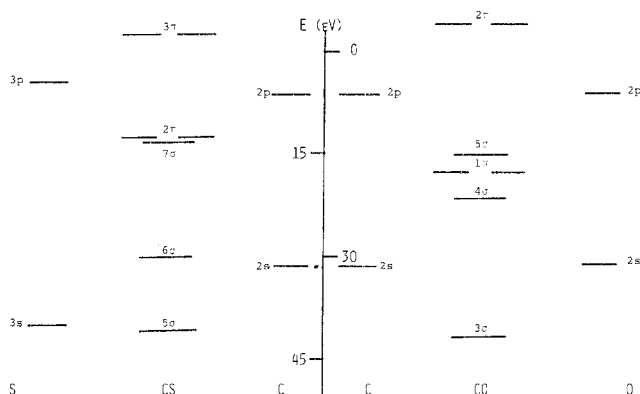


Figure 1. Molecular orbital diagrams for CO and CS (taken from ref 14). Ground-state configurations: CO, $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$; CS, $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 7\sigma^2 2\pi^4$.

selenocarbonyls and (2) to give a brief review of the physicochemical properties of these interesting new classes of organometallic complexes. Since many metal carbonyls have been used as reagents in organic synthesis¹⁹ and as homogeneous catalysts in industrial reactions,²⁰ it is anticipated that some metal thio- and selenocarbonyls may well find similar uses in the future. Indeed, several arenechromium thiocarbonyl derivatives have already been shown to be selective homogeneous catalysts for the isomerization of dienes.²¹ Finally, certain metal carbonyl thiocarbonyls may well find application as materials for chemical lasers since the active species in the CS₂/O₂ chemical laser are CO and CS.^{22,23}

Metal Thiocarbonyls

In general, binary metal carbonyls are prepared by the reactions of metals (e.g., Ni, Fe) or metal salts (e.g., Re₂O₇) with CO, usually under high pressure and at high temperature. In view of the instability of CS above -160 °C, this approach would not be viable for the synthesis of metal thiocarbonyls, and there is thus far only one example of the direct reaction of CS with a metal to afford a binary metal thiocarbonyl, viz., Ni(CS)₄.²⁴ This unstable species is apparently produced by the cocondensation of Ni atoms and CS (formed by passing a microwave discharge through CS₂ vapor) in an Ar matrix at 10 K.

As yet, there is no general synthetic route to metal thiocarbonyls containing terminal CS groups. However, there are several limited preparative methods known which utilize reagents such as CS₂, Cl₂CS, and ClC(S)OR (R = Me, Et) as sources of CS.

1. Direct Reaction with CS₂. The reactions of transition-metal complexes with CS₂ are often extremely complex, with products containing π -CS₂, S-bonded CS₂, and bridging CS₂ groups being formed as well as thiocarbonyls.⁸ In addition, CS₂ insertion reactions are fairly common. As will be indicated below, π -CS₂ complexes are often precursors to metal thiocarbonyls.

(19) For example, see G. Jaouen and R. Dabard, *Tetrahedron Lett.*, 1015 (1971), and references therein.

(20) For example, see A. J. Chalk and J. F. Harrod, *Organometal. Chem. Rev.*, **6**, 119 (1968), and references therein.

(21) G. Jaouen, personal communication.

(22) N. Djeu, *J. Chem. Phys.*, **60**, 4109 (1974).

(23) G. Kimbell, personal communication.

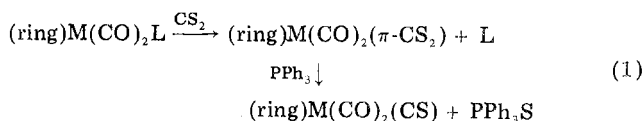
(24) G. V. Calder, J. G. Verkade, and L. W. Yarbrough II, *J. Chem. Soc., Chem. Commun.*, 705 (1973).

The *trans*-RhX(CS)(PPh₃)₂ (X = Cl, Br) complexes are produced by the direct reaction of RhX(PPh₃)₃ with CS₂ via π -CS₂ intermediates.^{25,26} Among the side products of the reactions is PPh₃S, and so it appears that the displaced PPh₃ ligand acts as the sulfur acceptor. The closely related iridium(I) species, *trans*-IrCl(CS)(PPh₃)₂, is best prepared by the reaction of *trans*-IrCl(N₂)(PPh₃)₂ with CS₂.²⁷

Successive treatment of $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2]^-$ (M = Fe,²⁸ Ru²⁹) with CS₂ and MeI yields the dithioesters, $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2\text{C}(\text{S})\text{SMe}$, which upon cleavage with HCl (Fe) or CF₃SO₃H (Ru) afford the cationic $[(\eta^5\text{-C}_5\text{H}_5)\text{M}(\text{CO})_2(\text{CS})]^+$ species. The dimeric, halogen-bridged $[\text{RuX}_2(\text{CS})(\text{PPh}_3)_2]_2$ (X = Cl, Br) complexes are produced by refluxing CS₂ solutions of RuX₂(PPh₃)₃ or RuX₂(PPh₃)₄.³⁰

Among the various products isolated from the reaction of Co₂(CO)₈ with CS₂ is a complex with the stoichiometry Co₃(CO)₆(CS₂).³¹ The tentative structure proposed for this complex incorporates a triangle of three Co(CO)₂ units bonded to an apical trivalent sulfur atom, while the CS group is bonded to the three cobalt atoms on the other side of the Co₃ cluster. As a final example of the direct reaction with CS₂, the ruthenium(III) thiocarbonyls, RuBr₃(CS)(EPh₃) (E = P, As), are obtained from the reactions of RuBr₃(EPh₃)₂MeOH with CS₂.³²

2. Reaction with CS₂/PPh₃. Since the presence of a suitable sulfur acceptor appears essential to the formation of certain metal thiocarbonyls, several studies have been carried out on the reactions of transition-metal complexes with CS₂ in the presence of PPh₃. For example, *trans*-IrCl(CS)(PPh₃)₂ can be prepared by the reaction of $[\text{IrCl}(\text{C}_8\text{H}_{12})_2]_2$ with CS₂/PPh₃.³³ Similar labile ligand displacements have been used extensively in the synthesis of group 6B and 7B metal thiocarbonyls (eq 1), where ring = $\eta^5\text{-C}_5\text{H}_5$, $\eta^5\text{-C}_5\text{H}_4\text{Me}$, $\eta^6\text{-C}_6\text{H}_6$, η^6 -



C₆H₅CO₂Me, etc; M = Cr,^{16,34} Mn,^{35,36} Re;³⁶ L = C₈H₁₄, THF. In the case of manganese, reaction 1 has been extended to give the di- and trithiocarbonyls, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{CS})_2$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CS})_3$, via the *cis*-cyclooctene precursors, $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})(\text{CS})(\eta^2\text{-C}_8\text{H}_{14})$ and $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CS})_2(\eta^2\text{-C}_8\text{H}_{14})$, respectively.³⁵ The related rhenium(I) dithiocarbonyl complex, $(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{CO})(\text{CS})_2$, has been identified spectroscopically.³⁵

(25) M. C. Baird and G. Wilkinson, *Chem. Commun.*, 267 (1966).

(26) M. C. Baird, G. Hartwell, and G. Wilkinson, *J. Chem. Soc. A*, 2037 (1967).

(27) M. Kubota and C. R. Carey, *J. Organometal. Chem.*, **24**, 491 (1970).

(28) B. D. Dombek and R. J. Angelici, *Inorg. Synth.*, **17**, in press.

(29) T. A. Wnuk and R. J. Angelici, *Inorg. Chem.*, in press.

(30) J. D. Gilbert, M. C. Baird, and G. Wilkinson, *J. Chem. Soc. A*, 2198 (1968).

(31) E. Klumpp, G. Bor, and L. Marko, *J. Organometal. Chem.*, **11**, 207 (1968).

(32) L. Ruiz-Ramirez, T. A. Stephenson, and E. S. Switkes, *J. Chem. Soc., Dalton Trans.*, 1770 (1973).

(33) M. Yagupsky and G. Wilkinson, *J. Chem. Soc. A*, 2813 (1968).

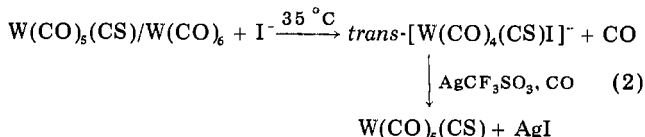
(34) G. Jaouen and R. Dabard, *J. Organometal. Chem.*, **72**, 377 (1974).

(35) A. E. Fenster and I. S. Butler, *Inorg. Chem.*, **13**, 914 (1974).

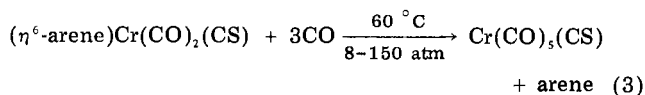
(36) I. S. Butler, N. J. Coville, and D. Cozak, *J. Organometal. Chem.*, **133**, 59 (1977).

3. Reaction with Thiophosgene (Cl₂CS).

Treatment of group 6B metal carbonyl anions, chiefly [M₂(CO)₁₀]²⁻ (M = Cr, Mo, W), produced by sodium amalgam reduction of M(CO)₆ in THF solution, with excess Cl₂CS gives low yields (usually <10%) of M(CO)₅(CS) contaminated with large amounts of M(CO)₆, which is regenerated in the reactions.³⁷ While repeated recrystallization does effect separation of M(CO)₅(CS) from M(CO)₆, a more efficient procedure, at least in the case of the tungsten complex, involves the chemical separation indicated in eq 2. The hexacarbonyl does



not react with I⁻ under these conditions. The use of ¹³CO affords the stereospecifically labeled species, *trans*-W(CO)₄(¹³CO)(CS).³⁸ A much higher yield synthesis of Cr(CO)₅(CS), involving the displacement of arene ligands from (η⁶-arene)Cr(CO)₂(CS) with CO under pressure (eq 3), has recently been discovered.³⁹

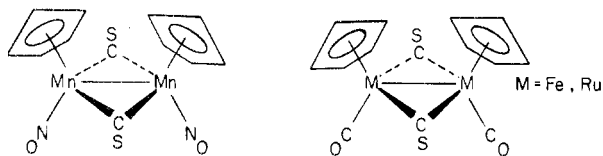


This method has the added advantage of not requiring separation of Cr(CO)₅(CS) from Cr(CO)₆. Thiophosgene has also been used as the in situ source of CS in the "three-fragment" oxidative additions of Cl₂CS to *trans*-IrCl(N₂)PPh₃₂ and [Ir(CO)(MeCN)(PPh₃)₂]⁺ to give IrCl₃(CS)(PPh₃)₂ and [IrCl₂(CO)(CS)(PPh₃)₂]⁺, respectively.⁴⁰

4. Reaction with Alkoxy Derivatives of Thiophosgene. Addition of ClC(S)OR (R = Me, Et) to [(η⁵-C₅H₅)Fe(CO)₂]⁻ yields the thiocarboxyl derivative (η⁵-C₅H₅)Fe(CO)₂C(S)OR, which upon treatment with HCl gives [(η⁵-C₅H₅)Fe(CO)₂(CS)]Cl.⁴¹ Similarly, reaction of Pt(PPh₃)₄ with ClC(S)OMe affords *trans*-PtCl[C(S)OMe](PPh₃)₂, which upon reaction with BF₃ yields *trans*-[PtCl(CS)(PPh₃)₂]⁺.⁴² The same complex is apparently also produced by the reaction of Pt(PPh₃)₃ or Pt(PPh₃)₂(η²-C₂H₄) with Cl₂CS.⁴⁰

Bridging Thiocarbonyl Complexes

It was mentioned earlier that CS can form both metal-C(S)-metal and metal-C≡S-metal bridges. In fact, it seems that CS may have a greater tendency to form ketonic-like bridges than does CO.²⁹ Two examples of complexes containing thioketonic bridges are shown. The manganese complex is formed by the



(37) B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, **15**, 1089 (1976).

(38) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **98**, 4110 (1976).

(39) A. M. English, K. R. Plowman, I. S. Butler, G. Jaouen, P. LeMaux, and J.-Y. Thépot, *J. Organometal. Chem.*, **132**, C1 (1977).

(40) M. Kubota and C. J. Curtis, *Inorg. Chem.*, **13**, 2277 (1974).

(41) L. Busetto and R. J. Angelici, *J. Am. Chem. Soc.*, **90**, 3283 (1968).

(42) R. J. Angelici, J. Clardy, E. D. Dobrzynski, and J. M. Lisey, *J. Am. Chem. Soc.*, **97**, 656 (1975).

Table I
IR Ranges of the ν(CX) Modes in the Known Types of Metal Thiocarbonyl and Selenocarbonyl Complexes

Type of complex	ν(CX), cm ⁻¹
Metal-CS ^a	1409-1161
Metal-C(S)-metal	1150-1118
Metal-C≡S-Metal	1106-1048
Metal-CSe ^b	1137-1063

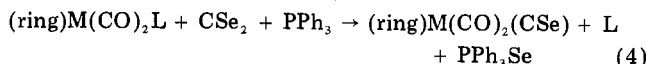
^a For "free" CS (trapped in a CS₂ matrix at -196 °C), ν(CS) is 1274 cm⁻¹ [R. Steudel, *Z. Naturforsch. B*, **21**, 1106 (1966)]. ^b For "free" CSe, ν(CSe) is 1036 cm⁻¹ (extrapolated value from the electronic spectrum; see ref 7).

reaction of (η⁵-C₅H₅)Mn(CS)(NO)I with Zn dust,⁴³ while the iron and ruthenium species are obtained by NaH reduction of [(η⁵-C₅H₅)M(CO)₂(CS)]⁺.^{13,29}

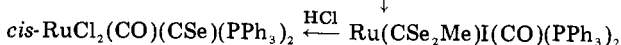
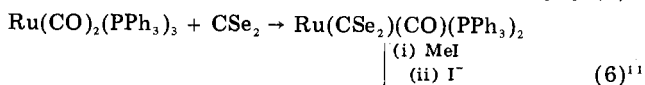
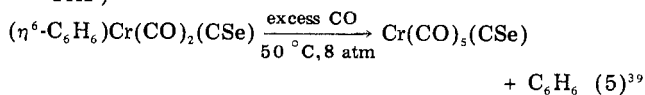
There are several examples of terminal CS groups bonding to another metal, e.g., (Diphos)₂(CO)W-C≡S-W(CO)₅ and [(Diphos)₂(CO)W-C≡S-]₂Ag⁺ (Diphos = Ph₂PCH₂CH₂PPh₂).^{44,45} These complexes are prepared by the reactions of W(CO)(CS)(Diphos)₂ with W(CO)₅(Me₂CO) and Ag⁺, respectively. There is spectroscopic evidence for the formation of the end-to-end CS bridged species, [(η⁵-C₅H₅)Mn(CO)₂]₂CS, during the reaction of (η⁵-C₅H₅)Mn(CO)₂(THF) with CS₂ in the absence of a sulfur acceptor.³⁶

Metal Selenocarbonyls

Only selenocarbonyl complexes containing terminal CSe groups have so far been synthesized. The preparative routes closely parallel those described above for the related metal thiocarbonyls; for example, see eq 4-6.



(ring = η⁵-C₅H₅, η⁶-C₆H₆, etc.; M = Cr, Mn, Re; L = C₆H₁₄, THF)¹⁰



It should be mentioned that recent work^{16,46} on the synthesis of chromium thio- and selenocarbonyls by reactions 1 and 4, respectively, has shown that better yields are obtained in the absence of PPh₃. Also, the synthesis of Cr(CO)₅(CSe) by a method comparable to the thiophosgene route, described earlier for the analogous group 6B metal thiocarbonyls, M(CO)₅(CS) (M = Cr, Mo, W), is impossible owing to the nonexistence of Cl₂CSe.

Physicochemical Properties of Metal Thio- and Selenocarbonyls

The most common spectroscopic technique used to identify metal thio- and selenocarbonyls is IR spec-

(43) A. Efraty, R. Arneri, and M. H. A. Huang, *J. Am. Chem. Soc.*, **98**, 639 (1976).

(44) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **96**, 7568 (1974).

(45) B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, **15**, 2397 (1976).

(46) I. M. Baibich, I. S. Butler, A. M. English, and K. R. Plowman, unpublished results.

Table II
Comparison of the Primary Stretching Force Constants
of $W(CO)_6$ and $W(CO)_5(CS)^a$

$W(CO)_6$		$W(CO)_5(CS)$	
f_{CO}	16.80 (2)	f_{CO}^{eq}	16.78 (2)
		f_{CO}^{ax}	16.88 (3)
		f_{CS}	8.17 (5)
f_{WC}	2.36 (4)	f_{WC}^{eq}	2.32 (2)
		f_{WC}^{ax}	2.12 (6)
		f_{WC}^s	2.77 (9)

^a For more details on the normal coordinate calculations, see ref 48 and L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, **8**, 2349 (1969).

troscopy. As for the $\nu(CO)$ modes in metal carbonyls, there are distinct ranges observed for the $\nu(CS)$ and $\nu(CSe)$ vibrations depending on the type of bonding involved (Table I). While there is some potential overlap in the regions, provided that the chemistry of the reactions being carried out is reasonably apparent, the nature of the CX groupings is readily ascertained from the IR spectra. In the case of terminal CX groups, the $\nu(CX)$ modes in metal chalcocarbonyls often appear above $\nu(CX)$ for the "free" diatomic CX molecules, in marked contrast to the $\nu(CO)$ modes in metal carbonyls which, with few exceptions,⁴⁷ are always at lower energy than $\nu(CO)$ for CO itself. For metal thiocarbonyls, this is partly due to the antibonding nature of the 7σ donor level of CS: σ donation effectively increases the bond order of the CS group. However, complete normal coordinate calculations have been carried out for $M(CO)_5(CS)$ ($M = Cr, W$) and *trans*- $W(CO)_4(^{13}CO)(CS)$, and it is clear that the discrepancy is also partly attributable to appreciable mixing of the $\nu(CS)$ modes with lower energy modes, particularly $\nu[M-C(S)]$.⁴⁸ Interestingly, the $\nu(CO)$ and $\nu(CS)$ modes are not appreciably mixed. The calculations also reveal that the "energy-factoring" approach commonly used to compute CO force constants is not viable for CS force constants. This will probably prove to be even more true for CSe force constants since the $\nu(CSe)$ modes are expected to be even more extensively mixed with the low-energy modes.

In the IR, terminal $\nu(CX)$ modes are of comparable intensity to $\nu(CO)$ modes. However, in the Raman, while $\nu(CSe)$ modes are moderately intense,⁴⁶ $\nu(CS)$ modes are extremely weak or nonexistent.^{9,48} The latter observation for metal thiocarbonyls is surprising because replacement of oxygen by the more polar sulfur atom would be expected to increase the polarizability of the CS bond compared to CO and hence to increase the intensity of the $\nu(CS)$ mode in the Raman.

Some of the force constants obtained from normal coordinate calculations on $W(CO)_6$ and $W(CO)_5(CS)$ are compared in Table II. Clearly, there is no effect on the equatorial CO and $W-C(O)$ force constants, f_{CO}^{eq} and f_{WC}^{eq} , in going from $W(CO)_6$ to $W(CO)_5(CS)$. However, there are significant changes in the corresponding axial force constants, f_{CO}^{ax} and f_{WC}^{ax} ; the former increases while the latter decreases. Furthermore, in agreement with the stronger metal-carbon bonding expected for metal-C(S) linkages, the $W-C(S)$ force constant, f_{WC}^s , is substantially larger than either of the $W-C(O)$ force

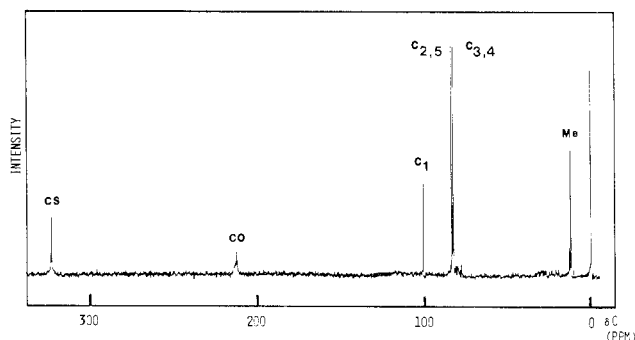


Figure 2. ^{13}C NMR spectrum of $(\eta^5-C_5H_4Me)Mn(CO)(CS)_2$. Conditions: neat liquid (D_2O capillary), 9090-Hz sweep width, 3.0-s repetition rate, 5700 scans, 30° flip angle (taken from ref 16).

constants. Similar results are observed for the chromium complex, $Cr(CO)_5(CS)$.⁴⁸ The weakening of the $M-C(O)$ bonds *trans* to CS in $M(CO)_5(CS)$ ($M = Cr, W$) is believed to be chiefly due to the stronger π -acceptor capacity of the CS ligand. Indeed, absolute integrated IR intensity measurements on the $\nu(CO)$ and $\nu(CS)$ modes in $(\eta^5-C_5H_5)Mn(CO)_2(CS)$ ⁴⁹ and Mössbauer studies⁵⁰ on $[(\eta^5-C_5H_5)Fe(CO)_2(CS)]^+$ provide further support for the greater π acidity of CS.

It was mentioned earlier that PES measurements have been reported for several metal thiocarbonyls, viz., $M(CO)_5(CS)$ ($M = Cr, W$) and $(\eta^5-C_5H_5)Mn(CO)_2(CS)$.¹⁴ The ionizations associated mainly with the highest occupied σ and π levels of the CS ligand are clearly separated from the other ionizations and exhibit distinctly different band envelopes. These results, together with molecular orbital calculations for the chromium and manganese species, reveal that CS is a much better π -acceptor ligand than CO and a slightly better σ -donor ligand. Moreover, in addition to the expected $\sigma + \pi$ synergistic interaction, there is an appreciable interaction between the occupied π levels of the CS ligand and the metal. The net result of these interactions is a buildup of electron density at the carbon atom of the CS group. These molecular orbital calculations also provide an explanation for the low Raman intensity of $\nu(CS)$ modes. The closer the proximity of the empty CS π^* orbitals and the occupied π orbitals, the greater the polarizability. However, CS stretching lowers the energy of the π^* orbitals and increases their carbon character, thereby increasing their interaction with the metal. At the same time, the CS π levels are destabilized by stretching, but they also acquire less carbon character, and so their interaction with the metal is decreased. These two competing effects will result in a decrease in the change of polarizability for the CS bond and so reduce the intensity of the vibration in the Raman, as is observed.

Some data have been reported for the ^{13}C NMR chemical shifts of the CX ligands in series of metal chalcocarbonyl complexes, e.g., $(\eta^5-C_5H_5)M(CO)_2(CX)$ ($M = Mn, Re$),¹⁵ $(\eta^6\text{-arene})Cr(CO)_2(CX)$,¹⁶ and $[(\eta^5-C_5H_5)Fe(CO)(CS)L]^+$ [$L = PPh_3, P(C_6H_4F)$, etc.].⁵¹ The ^{13}C peaks are at extremely low fields, comparable to those found for metal carbene complexes,⁵² and it is

(49) I. S. Butler and D. A. Johansson, *Inorg. Chem.*, **14**, 701 (1975).

(50) K. Burger, L. Korecz, P. Mag, U. Belluco, and L. Busetto, *Inorg. Chim. Acta*, **5**, 362 (1971).

(51) L. Busetto and A. Palazzi, *Inorg. Chim. Acta*, **19**, 233 (1976).

(52) J. A. Connor, E. M. Jones, E. W. Randall, and E. Rosenberg, *J. Chem. Soc., Dalton Trans.*, 2419 (1972).

(47) Y. Souma, J. Iyoda, and H. Sano, *Inorg. Chem.*, **15**, 968 (1976).

(48) I. S. Butler, A. Garcia-Rodriguez, K. R. Plowman, and C. F. Shaw III, *Inorg. Chem.*, **15**, 2602 (1976).

Table III
¹³C NMR Spectra (ppm) of Some (Ring)M(CO)₃ and
 (Ring)M(CO)₂(CX) Complexes

Complex	δ(C _n H _n)	δ(CO)	δ(CX)
(η ⁵ -C ₅ H ₅)Mn(CO) ₃	83.0	224.5	
(η ⁵ -C ₅ H ₅)Mn(CO) ₂ (CS)	86.3	224.0	335.4
(η ⁵ -C ₅ H ₅)Mn(CO) ₂ (CSe)	86.9	223.1	357.2
(η ⁵ -C ₅ H ₅ Me)Mn(CO) ₃	b	225.4	
(η ⁵ -C ₅ H ₄ Me)Mn(CO) ₂ (CS)	c	223.9	336.6
(η ⁵ -C ₅ H ₄ Me)Mn(CO) ₂ (CSe)	d	223.0	358.8
(η ⁶ -C ₆ H ₆)Cr(CO) ₃	93.7	233.4	
(η ⁶ -C ₆ H ₆)Cr(CO) ₂ (CS)	99.3	231.5	346.4
(η ⁶ -C ₆ H ₆)Cr(CO) ₂ (CSe)	100.8	229.4	363.3

^a The values are accurate to ±0.1 ppm and are downfield from Me₄Si. The data are from ref 15, 16, and 46.

^b δ C(ring): 102.7 (C₁), 82.4 (C_{2,s}), 82.0 (C_{3,4}), 13.3 (Me). ^c δ C(ring): 104.4 (C₁), 85.5 (C_{2,s}), 84.4 (C_{3,4}), 13.3 (Me). ^d δ C(ring): 105.5 (C₁), 86.8 (C_{2,s}), 85.5 (C_{3,4}), 13.0 (Me).

often necessary to resort to low temperatures in order to locate the resonances definitively. The spectrum of liquid (η⁵-C₅H₄Me)Mn(CO)(CS)₂ is shown in Figure 2 to illustrate the typical positions of the CS and CO resonances. The current ranges for the CX resonances (downfield from Me₄Si) are: δ(¹³CS) 286–352; δ(¹³CSe) 308–363 ppm. The ¹³C NMR data reflect the difference between the CX ligands and other monodentate ligands (L) because replacement of a CO group in complexes such as (η⁵-C₅H₅)Mn(CO)₃ to give (η⁵-C₅H₅)Mn(CO)₂L invariably produces a downfield chemical shift for δ(¹³CO),⁵³ whereas replacement by CX affords an upfield chemical shift (Table III). Furthermore, on the basis of the CO chemical shifts, CSe appears to be a better net electron-withdrawing (σ donor vs. π acceptor) group than CS.

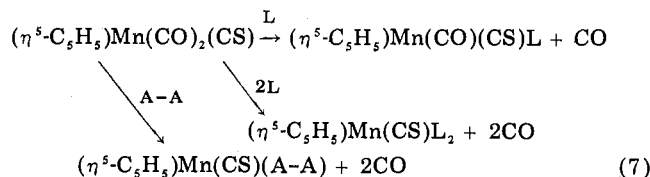
Although only a few x-ray studies on terminal metal chalcocarbonyls complexes have been reported,^{11,12} there is a definite shortening in the metal–CX distances compared to those for metal–CO bonds, in accord with the stronger bonding expected for the former. On the basis of the usual π-bonding arguments, thiocarbonyl complexes with low terminal ν(CS) frequencies would be expected to have long C–S bonds. This is indeed true, and a linear correlation between ν(CS) and C–S bond distance has been reported.¹²

The stronger bonding of metal–CX linkages compared to metal–CO ones also appears to be evident in the mass spectra of metal chalcocarbonyl complexes. One of the prominent ions is always metal–CX⁺, and loss of CO invariably precedes loss of CX.^{16,39,54–56} For example, the initial fragmentation of Cr(CO)₅(CX) is Cr(CO)₅(CX)⁺ → Cr(CO)₃(CX)⁺, and this is followed by stepwise loss of CO to give Cr(CX)⁺.³⁹ The use of appearance potential data to discuss the bonding in metal thiocarbonyls seems hazardous since conflicting opinions have resulted. In the case of (η⁵-C₅H₄R)Mn(CO)₂(CX) (R = H, Me),⁵⁵ the data suggested that CS is primarily a σ-donor ligand, while for (η⁶-C₆H₅CO₂Me)Cr(CO)(CS)L [L = CO, P(OEt)₃, P(OPh)₃],⁵⁶ the results could be interpreted unambig-

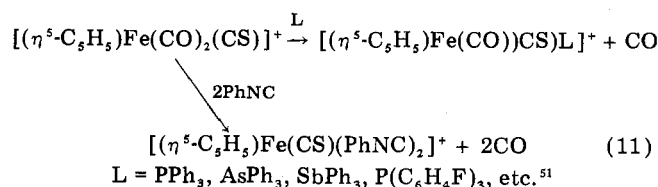
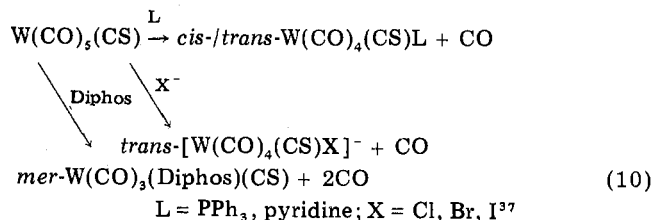
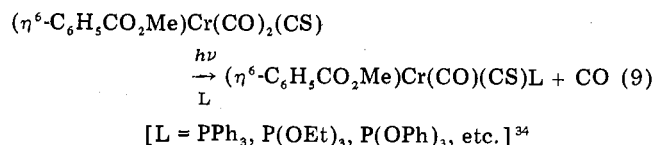
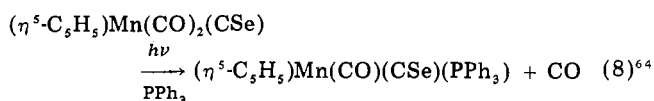
uously in terms of the greater σ-donor and π-acceptor abilities of CS compared to CO. The ionization energy of (η⁵-C₅H₅)Mn(CO)₂(CS) (7.78 eV) is less than that of (η⁵-C₅H₅)Mn(CO)₃ (8.06 eV), whereas that of the chromium complex (η⁶-C₆H₅CO₂Me)Cr(CO)₂(CS) (7.8 eV) is greater than that of (η⁶-C₆H₅CO₂Me)Cr(CO)₃ (7.1 eV).

It has recently been suggested that the apparent disparity in the electronic properties of CS compared to CO, depending on the system being studied and the spectroscopic method utilized, is attributable to the fact that the π-acceptor to σ-donor ratio varies more for CS than for CO.⁵⁷ This is supported by the greater variation found for C–S bond lengths in metal thiocarbonyls than for C–O bond lengths in metal carbonyls.¹² It appears that there is a crossover in the relative electronic properties of CS and CO which can be correlated semiquantitatively with the CO stretching force constant of the parent carbonyl complex. Essentially, when *k*_{CO} of the parent carbonyl complex is less than 17.1 mdyn/Å, the π acceptor to (σ + π)⁵⁸ ratio is greater for CS than for CO; when *k*_{CO} > 17.1 mdyn/Å, however, this ratio is lower for CS than for CO.

In general, metal–CX bonds are much stronger with respect to nucleophilic substitution at the metal than are metal–CO bonds. Numerous thermal and photochemical substitution studies have been carried out using both mono- and polydentate ligands (e.g., eq 7–11). Similar reactions to eq 9 have been used re-



L = PPh₃, SbPh₃, P(OPh)₃, C₈H₁₄, SMe₂, C¹⁸O, NO⁺, etc;
 A–A = Diphos, Triphos [PhP(CH₂CH₂PPh₂)₂]^{35,59–63}



(53) G. M. Bodner, *Inorg. Chem.*, **13**, 2563 (1974).

(54) I. S. Butler, N. J. Coville, A. Garcia-Rodriguez, A. E. Fenster, T. Sawai, and S. R. Stobart, unpublished results.

(55) A. Efraty, M. H. A. Huang, and C. A. Weston, *Inorg. Chem.*, **14**, 2796 (1975).

(56) G. Simonneaux, G. Jaouen, R. Dabard, and P. Guenot, submitted for publication.

(57) M. A. Andrews, *Inorg. Chem.*, **16**, 496 (1977).

(58) The fact that CS can act as a π-donor ligand is included here.

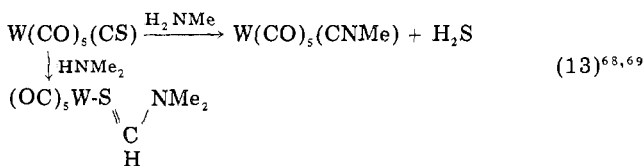
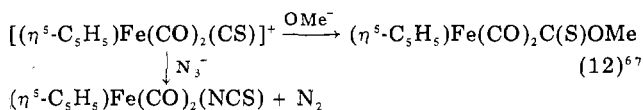
(59) N. J. Coville and I. S. Butler, *J. Organometal. Chem.*, **64**, 101 (1974).

(60) I. S. Butler and N. J. Coville, *J. Organometal. Chem.*, **80**, 235 (1974).

cently to produce the first examples of resolved enantiomeric chromium(0) complexes.⁶⁵ These complexes may well prove to be useful catalysts for asymmetric organic synthesis.

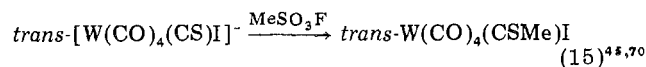
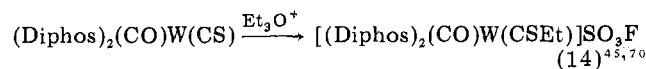
In the reaction of *trans*-W(CO)₄(¹³CO)(CS) with I⁻, ¹³C NMR studies have shown that there is stereochemical preference for substitution of the labeled CO to give *trans*-[W(CO)₄(CS)I]⁻.³⁸ Ultraviolet photolysis of M(CO)₅(CS) (M = Cr, W) under matrix isolation conditions at 20 K yields a mixture of two isomeric forms of M(CO)₄(CS) and molecular CO.⁶⁶ Both isomers have square-pyramidal structures: axial CS (C_{4v} symmetry) and basal CS (C_s symmetry).

There is also some evidence for nucleophilic attack occurring at the carbon atom of the CS group in certain metal thiocarbonyls, e.g., eq 12 and 13. Other com-



plexes in which the thiocarbonyl carbon atom apparently exhibits electrophilic character include $[(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2(\text{CS})]^+$ and *trans*-[PtCl(CS)(PPh₃)₂]⁺.⁴ In the case of W(CO)₅(CS), it has been pointed out that nucleophilic attack of amines at the thiocarbonyl carbon atom seems contrary to the expected increase of electron density at this carbon center.¹⁴ In view of this, it was suggested that these reactions were frontier controlled rather than charge controlled. Whether this is a general phenomenon for these metal thiocarbonyl complexes remains to be established.

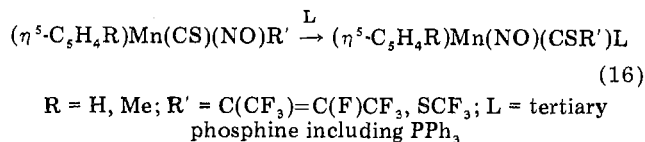
Several thiocarbonyl complexes have been observed to undergo reaction with organic electrophiles, e.g., eq 14 and 15. These complexes represent the first known



examples of the *S*-alkylthiocarbonylium ligand, CS-R⁺. The formation of -C≡S- bridged species such as [(Diphos)₂(CO)W(CS)]₂Ag⁺ can also be regarded as reactions of thiocarbonyl complexes with electrophiles.^{44,45} In any event, it seems that only those complexes having ν(CS) below 1200 cm⁻¹ are reactive

toward electrophiles. The bridging thiocarbonyl complex, *cis*-[(η⁵-C₅H₅)Fe(CO)(CS)]₂, reacts with MeSO₃F to give the cationic species, [(η⁵-C₅H₅)₂Fe₂(CO)₂(CS)(CSMe)]⁺, which contains a methylated bridging thiocarbonyl group and not the *S*-methylthiocarbonylium ligand, CS-Me⁺.¹³

There are now several examples of intramolecular insertion of a coordinated CS ligand (eq 16).⁷¹



Kinetic studies often provide valuable information concerning the bonding properties of coordinated ligands in transition-metal complexes. However, only three kinetic investigations of ligand substitution reactions in metal thiocarbonyl complexes have so far been reported. In the case of (η⁵-C₅H₅)Mn(CO)(CS)-(η²-C₈H₁₄),⁷² replacement of *cis*-cyclooctene by PPh₃ proceeds by an S_N1 dissociative mechanism involving the formation of the (η⁵-C₅H₅)Mn(CO)(CS) intermediate. This 16-electron species has been detected by IR spectroscopy during the UV irradiation of (η⁵-C₅H₅)Mn(CO)₂(CS) trapped in a glass matrix at -196 °C.⁷³ The rate constant for the thiocarbonyl complex is about four times greater than that for the analogous reaction of (η⁵-C₅H₅)Mn(CO)₂(η²-C₈H₁₄) with PPh₃ under the same conditions. On the other hand, the CO substitution reactions of W(CO)₅(CS) with PPh₃ and I⁻ are appreciably faster than the corresponding reactions of W(CO)₆.³⁷ The reaction with PPh₃ follows a mixed-order (S_N1 + S_N2) mechanism, while the reaction with I⁻ proceeds via a purely S_N2 associative mechanism. For PPh₃, the dissociative pathway is approximately 75 times faster than that for W(CO)₆, while the associative pathway is about 250 times faster. In the case of I⁻, W(CO)₅(CS) reacts more than 1000 times faster than does W(CO)₆. The apparent disparity in rate enhancement between manganese and tungsten was accounted for in the following way. The presence of the electron-releasing cyclopentadienyl ligand in the manganese complex might lower the activating effect of the CS ligand toward π-bonding dissociation; also, the *cis*-cyclooctene ligand is being effectively lost from a position *cis* to CS. For tungsten the larger rate acceleration observed for the first-order CO loss from W(CO)₅(CS) may have been due to its position *trans* to the CS group.

Future Prospects

It is evident that the chemistry of transition-metal chalcocarbonyls will continue to be a fertile area of research. This is particularly true of metal selenocarbonyls where the synthesis of complexes such as Cr(CO)₅(CSe) opens up many new avenues of research. Hopefully, it will be possible to extend reaction 5 to the preparation of other group 6B metal M(CO)₅(CSe) complexes provided that suitable (η⁶-arene)M(CO)₂(CSe) precursors can be synthesized. Metal chalcocarbonyls are quite similar in many respects to metal

(61) A. Garcia-Rodriguez, M.Sc. Thesis, McGill University, Montreal, Quebec, Canada, 1974.

(62) I. S. Butler and A. E. Fenster, *J. Organometal. Chem.*, **51**, 307 (1973).

(63) A. Efraty, R. Arneri, and J. Sikora, *J. Organometal. Chem.*, **91**, 65 (1975).

(64) I. S. Butler and L. Gontavnick, unpublished results.

(65) G. Simonneaux, A. Meyer, and G. Jaouen, *J. Chem. Soc., Chem. Commun.*, 69 (1975).

(66) M. Poliakoff, *Inorg. Chem.*, **15**, 2022 (1976).

(67) L. Busetto, M. Graziani, and U. Belluco, *Inorg. Chem.*, **10**, 78 (1971).

(68) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **95**, 7516 (1973).

(69) B. D. Dombek and R. J. Angelici, *Inorg. Chem.*, **15**, 2403 (1976).

(70) B. D. Dombek and R. J. Angelici, *J. Am. Chem. Soc.*, **97**, 1261 (1975).

(71) A. Efraty, personal communication.

(72) I. S. Butler and A. E. Fenster, *Inorg. Chim. Acta*, **7**, 79 (1973).

(73) P. S. Braterman and J. D. Black, unpublished results.

carbonyls, but the subtle differences in their bonding properties lead to many interesting reactions. One major difference between metal carbonyls and metal thio- and selenocarbonyls is the present scarcity of complexes containing multiple CS and CSe groups. It is probable that future research may well show that these types of complexes are difficult to obtain because of the destabilizing effects resulting from the strong π -acceptor capacities of the CS and CSe ligands. Finally, since it has been demonstrated that various metal chalcocarbonyl complexes can be prepared, it is anticipated that the catalytic potential of these complexes

will become an important research area. The optically active chromium complexes, $(\eta^6\text{-arene})\text{Cr}(\text{CO})(\text{CS})\text{L}$, are particularly promising as catalysts for asymmetric organic synthesis.

It is a pleasure to acknowledge the contributions to this research area of my past and present students (I. M. Baibich, G. G. Barna, N. J. Coville, D. Cozak, A. M. English, A. E. Fenster, A. Garcia-Rodriguez, L. Gontavnick, D. A. Johansson, T. Sawai) and postdoctoral fellows (K. R. Plouman, C. F. Shaw III). The research was generously supported by grants from the National Research Council of Canada and le Gouvernement du Québec (Ministère de l'Éducation).

Noncovalent Interactions

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The purpose of this Account is to show the interplay between theory and experiment in studies of noncovalent interactions. We define noncovalent interactions as those in which: (1) electrons stay paired in reactants and products and (2) there is no change in the type of chemical bonding in reactants and products. $\text{He}\cdots\text{He}$, $\text{H}_2\text{O}\cdots\text{H}_2\text{O}$, $\text{BH}_3\cdots\text{NH}_3$, and $\text{FH}\cdots\text{F}^-$ are examples of such interactions. We hope to show the reader the important role that theory continues to play in studies of these noncovalent interactions, which are responsible for many of the *physical* properties of condensed phases of matter.

We feel that the theory has two roles in chemistry: first, to provide quantitative predictions of phenomena; and second, to provide a language to enable one to interpret the large body of chemical facts.¹ We feel the study of noncovalent interactions is currently very exciting because, unlike the studies of covalent bonds, theory has often led experiment in studies of noncovalent bonding. For example, the structures of water dimer, $(\text{H}_2\text{O})_2$, and hydrogen fluoride dimer, $(\text{HF})_2$, were predicted rather well by the theory. In addition, the "intrinsic" structure of noncovalent bonds is much harder to characterize because these bonds are weaker and much more sensitive to environment than covalent bonds. Thus, an average chemist's insight into the nature of these bonds is still far behind his understanding of covalent bonding.

Theoretical and Experimental Methodology

To be able to treat intermolecular potentials in a reasonable way, all methods must include "quantum-mechanical" effects implicitly or explicitly, since the Pauli exchange repulsion plays a crucial role in keeping

two closed-shell molecules from approaching each other too closely. An intermolecular potential can only be defined within the Born-Oppenheimer approximation, which assumes that the nuclei move in an "effective" potential which contains both the nuclear-nuclear repulsions and the electronic terms (electronic kinetic energy, electron-electron repulsion, and nuclear-electron attraction). One expects that the Born-Oppenheimer approximation² and the neglect of relativistic and fine structure effects³ in treating intermolecular interactions are an excellent approximation for analyzing the energy and structure of intermolecular complexes.

Quantum mechanical studies of intermolecular interactions have predominately used the "supermolecule" approach (see, however, ref 4 and 5). This approach uses direct solutions to the Schroedinger equation (with a single or multideterminant wave function whose orbitals are usually a linear combination of atomic-based functions) for both complex and isolated fragments. This should be the method of choice for relatively "small" complexes, where quantitative predictions are of importance. Recently, Morokuma⁶ and others⁷ have broken down the interaction energy into components which correspond closely to the different energy components of a perturbation theory expansion. These energy components are electrostatic,

(1) These roles are eloquently described by Parr (R. G. Parr, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 763 (1976)).

(2) R. J. Cross, *Acc. Chem. Res.*, **8**, 225 (1975).

(3) For more detailed description of the calculation of such effects, see H. F. Schaefer, "The Electronic Structure of Atoms and Molecules: A Survey of Rigorous Quantum Mechanical Results", Addison-Wesley, Reading, Mass., 1972.

(4) For perturbation theory approaches to intermolecular complex formation, see J. C. G. M. van-Duijneveldt-van de Rijdt and F. B. van Duijneveldt, *J. Am. Chem. Soc.*, **93**, 5644 (1971).

(5) See, for example, Y. S. Kim and R. G. Gordon, *J. Chem. Phys.*, **61**, 1 (1974), G. A. Parker, R. L. Snow, and R. T. Pack, *ibid.*, **64**, 1668 (1976), and Quantum Chemistry Program Exchange Program No. 305 for an interesting modified Thomas-Fermi approach to studying intermolecular complexes.

(6) K. Morokuma, *J. Chem. Phys.*, **55**, 1236 (1971).

(7) See P. Kollman, "Hydrogen Bonding and Donor Acceptor Interactions", in "Modern Theoretical Chemistry", Vol. 4, H. F. Schaefer, Ed., Plenum Press, in press, for detailed descriptions of this.

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