

# Transition-Metal Dihalocarbene Complexes

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Received February 16, 1988 (Revised Manuscript Received May 27, 1988)

## Contents

I. Introduction	1293
II. Bonding	1294
III. Synthesis	1298
A. Trihalomethyl Complexes	1298
B. Dihalocarbene Complexes	1302
C. Monohalocarbene Complexes	1304
IV. Structural and Spectroscopic Properties	1306
A. Structural Results	1306
B. IR Spectroscopy	1308
C. NMR Spectroscopy	1309
V. Reactivity	1312
A. Control of Metal Carbene Reactivity	1312
B. Electrophilic Reactivity at the Carbene Carbon	1313
C. Nucleophilic Reactivity at the Carbene Carbon Atom	1319
D. Substitution at the Metal Center	1320
E. Halide Abstraction and Migration	1321
F. Redox Chemistry	1322
VI. Halocarbyne and Bridging Halocarbene Complexes	1322
A. Homobimetallic Complexes	1322
B. Heterobimetallic Complexes	1323
C. Structural Results	1323
D. Spectroscopic Results	1323
E. Halocarbyne Complexes	1324
VII. Conclusions	1324
VIII. Acknowledgment	1325
IX. References	1325

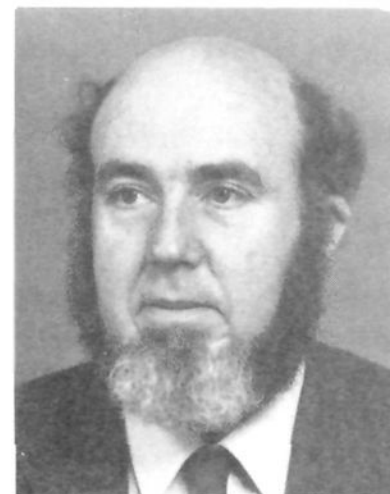
## I. Introduction

The quest to rationalize the diverse structural properties and reactivity patterns exhibited by transition-metal carbene complexes continues to challenge synthetic, structural, and theoretical chemists. This interest was sparked in 1975 when the first alkylidene complex to be reported,  $\text{Cp}_2\text{Ta}(=\text{CH}_2)(\text{CH}_3)$ ,<sup>1</sup> demonstrated nucleophilic reactivity at the carbene carbon atom. This was remarkably different from the electrophilic reactivity observed for carbene complexes like  $\text{W}(=\text{C}(\text{OMe})\text{Ph})(\text{CO})_5$ , first prepared over a decade earlier.

The early "black and white" classification of transition-metal carbene complexes as "Fischer-type" late-transition-metal carbenes with heteroatom substituents, or "Schrock-type" early-transition-metal alkylidenes with alkyl substituents, is yielding to a more sophisticated understanding of the factors that determine the reactivity of organometallic species. Theories of frontier orbital control versus electronic charge control of the reactions of carbene and alkylidene complexes, and more recently, a valence-bond approach recognizing the role played by the singlet or triplet ground state of the



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metal complex fragment and free carbene ligand in determining the nature of the bonding between the two fragments, have advanced our understanding of this chemistry. It is now apparent that a single, unified model for the bonding in metal carbene complexes is sufficient to rationalize the observed diversity in the chemistry.

In particular, the chemistry of transition-metal methylene and dihalocarbene complexes has been important in closing the gap between the two groups of carbene complexes previously thought to be distinct. For both these types of ligand, variation of the metal and the ancillary ligands in the complex can alter the reactivity of the carbene carbon center from electrophilic to nucleophilic. In the special case of ruthenium difluorocarbene complexes, a change in the oxidation state of the metal is sufficient to tip the balance.

Although transition-metal carbene chemistry has been reviewed extensively in recent years,<sup>2,4-9</sup> dihalocarbene complexes have received only passing comment within reviews with much wider scope.<sup>6,7</sup> The chemistry of these complexes has developed rapidly in the decade since the first dichlorocarbene complex was reported in 1977.<sup>10</sup> This fact and the contribution made by the conclusions drawn from this chemistry to our emerging understanding of the broad pattern of carbene reactivity warrant a review entirely devoted to detailing the development and scope of transition-metal dihalocarbene complexes.

A factor that is important both in stabilization and in determining the reactivity of a carbene complex is the extent of  $\pi$  donation from the carbene substituents to the carbene carbon atom. It is not surprising that the first carbene complexes to be prepared bore carbene substituents with good  $\pi$ -donor properties (OR, NR<sub>2</sub>) capable of stabilizing the reactive carbene carbon center. If the metal-carbon bond involves  $\sigma$  donation from the carbon to the metal and  $\pi$  back-donation in the other direction, as proposed for carbene complexes with heteroatom substituents, then  $\pi$  donation from the carbene substituent will compete with  $\pi$  donation from the metal. In alkylidene complexes, where  $\pi$  donation from the substituent is not significant, the metal-carbon bond will be more covalent in nature. As the electronegativity of the element increases along the series N, O, F, so the capability for  $\pi$  bonding decreases. Thus the dihalocarbene complexes, with electronegative heteroatom substituents but without significant  $\pi$  interaction between the carbene substituents and the carbene carbon, comprise a category intermediate between alkylidene species and the classical heteroatom-substituted (N, O, S, Se) carbene complexes. A unified model for the bonding in carbene complexes, and the contribution made by dihalocarbene complexes in developing and illustrating this model, will be outlined in section II.

Unlike methylene species, of which there are now examples involving both early<sup>1</sup> and late<sup>11,12</sup> transition metals, the dihalocarbene complexes reported to date are restricted to the middle and later transition elements. The bonding model outlined in section II does provide a justification for this. However, the key to these complexes lies in the availability of suitable synthetic routes, which are still relatively limited in scope for dihalocarbene species. One feature that arises from a survey of the available syntheses is the predominance of both transition-metal and main-group-metal trifluoromethyl species either as precursors to dihalocarbene complexes or as sources of the dihalocarbene fragment. This chemistry will be reviewed as part of the survey of synthetic routes to dihalocarbene complexes presented in section III. In addition, the scope

of this review has been extended to cover monohalocarbene complexes, which are important both as derivatives of dihalocarbene species and because in many ways the chemistry of mono- and dihalocarbene complexes is complementary. The structural and spectroscopic properties of the complexes reviewed here will be summarized in section IV.

Dihalocarbene complexes are unique in bearing two excellent leaving groups as the carbene substituents. This factor renders these complexes particularly useful for the synthesis of new organometallic species by modification of the carbene ligand. Nucleophilic substitution at the carbene center produces a rich selection of mono- and disubstituted carbene ligands, the former adding to a selection of monohalocarbene complexes produced by other routes. The first homologous series of transition-metal chalcogenide complexes, including the first example of a tellurocarbonyl ligand, was produced from an osmium dichlorocarbene complex.<sup>13</sup> Other reactions include the transformation of the carbene ligand to isocyanide and carbyne ligands and the production of metallacyclic species resulting from intramolecular electrophilic aromatic substitution. Both the above examples of electrophilic reactivity at the carbene ligand, several cases of nucleophilic reactivity at this site, and a migratory insertion reaction will be discussed in section V. These reactions of mono- and dihalocarbene species, as well as illustrating the synthetic utility of the ligand, offer an insight into the effect of the metal, metal oxidation state, carbene substituents, ancillary ligands, and complex charge on the reactivity.

Very few examples of bridging dihalocarbene species are known, and again the bonding model outlined in section II suggests an explanation. The few complexes that have been reported and the even more rare halocarbyne species are reviewed briefly in section VI. Brief conclusions are drawn in section VII.

Table I surveys the diversity of mono- and dihalocarbene complexes reported to date, with an example from each major class. This is intended as background for section II, to provide a context for the bonding arguments discussed here. Table III lists all the mono- and dihalocarbene complexes reviewed here and may be useful as a key while reading the text. Similarly, halocarbyne and bridging halocarbene species are tabulated in Table X.

## II. Bonding

An early classification of transition-metal carbene complexes was into two categories, according to reactivity at the carbene carbon atom. The first contained the "Fischer-type" complexes, characterized by electrophilic reactivity of the carbon center such as olefin cyclopropanation or Lewis base adduct formation. The second class comprised the "Schrock-type" complexes, which display nucleophilic reactivity. Typical reactions are olefin metathesis, Lewis acid adduct formation, and Wittig-type alkylations. As the area of metal carbene chemistry has developed, however, so has the need for a coherent, unified picture of bonding in all metal carbene species to account for the observed spectrum of chemical behavior.

Dihalocarbene complexes have a special role to play in this picture. The "Fischer-type" complexes are

TABLE I. Survey of Dihalocarbene and Monohalocarbene Complexes

dihalocarbene complexes		ref	monohalocarbene complexes		ref
d <sup>4</sup> group 6	[CpMo(=CF <sub>2</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub>	73	[CpMo(=C(F)C <sub>2</sub> F <sub>5</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub>		73
d <sup>6</sup> group 6			Cr(=C(Cl)NEt <sub>2</sub> )(CO) <sub>5</sub>		88
d <sup>6</sup> group 7	[Mn(=CF <sub>2</sub> )(CO) <sub>5</sub> ]BF <sub>4</sub>	31	CpMn(=C(F)Ph)(CO) <sub>2</sub>		84
			CpRe(=C(Cl)Ph)(CO) <sub>2</sub>		85
d <sup>6</sup> group 8	[CpFe(=CF <sub>2</sub> )(CO) <sub>2</sub> ]BF <sub>4</sub>	31			
	Fe(TPP)(=CCl <sub>2</sub> )	10	Fe(TPP)(=C(Cl)CO <sub>2</sub> Et)		95
	RuCl <sub>2</sub> (=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	23	RuCl <sub>2</sub> (C(F)OMe)(CO)(PPh <sub>3</sub> ) <sub>2</sub>		23
	OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	13	OsCl <sub>2</sub> (=C(Cl)- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub>		83
	[OsCl(=CFCl)(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub>	77	[OsCl(=C(F)NMe <sub>2</sub> )(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]SbF <sub>6</sub>		77
d <sup>6</sup> group 9	IrCl <sub>3</sub> (=CCl <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	25	IrCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>		25
d <sup>8</sup> group 8	Ru(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	76			
	OsCl(NO)(=CF <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub>	7			
d <sup>8</sup> group 9	Ir(CF <sub>3</sub> )(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	37			
bridging halocarbene complexes		ref	halocarbene complexes		ref
homobimetallic	( $\mu$ -CF <sub>2</sub> ) <sub>2</sub> [Mn(CO) <sub>4</sub> ] <sub>2</sub>	129	Mo(=CCl)(CO) <sub>2</sub> L <sup>a</sup>		135
	( $\mu$ -SMe) <sub>2</sub> ( $\mu$ -CF <sub>2</sub> )[Fe(CO) <sub>3</sub> ] <sub>2</sub>	131	ClC[Co(CO) <sub>3</sub> ] <sub>3</sub>		137
heterobimetallic	[CpFe(CO)( $\mu$ -CO)( $\mu$ -CF <sub>2</sub> )Ir(CO)(PMe <sub>2</sub> Ph) <sub>2</sub> ]BF <sub>4</sub>	121			
	Ru(CF <sub>2</sub> AuI)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	76			

<sup>a</sup>L = tetrakis(1-pyrazolyl) borate.

generally late-transition-metal species with heteroatom substituents (N, O), which are good  $\pi$  donors. This  $\pi$ -donation effect obviously plays an important role by stabilizing the electrophilic carbene center and also by competing with  $\pi$  donation from the low-valent metal center, thus affecting the nature of the metal-carbon bond. In contrast, the "Schrock-type" complexes are typically high-valent, early-transition-metal species with H or alkyl substituents, which have no significant substituent  $\pi$ -donation effects. Dihalocarbene complexes represent an intermediate case in this scheme. As electronegativity increases in the series N, O, F,  $\pi$ -donor ability decreases in the same order. In other respects, the dihalocarbene complexes reported to date are similar to their N- or O-substituted analogues, involving the later, low-valent metals. Thus they represent a class of heteroatom-substituted complexes where  $\pi$ -donor effects are of much reduced significance and in this sense can be compared to the "Schrock-type" complexes.

Dihalocarbene complexes are also significant in that they include examples where the same ligand (CF<sub>2</sub>) bonded to the same metal (Ru) exhibits reactivity dependent on the oxidation state of the metal. Ru<sup>II</sup>=CF<sub>2</sub> complexes are electrophilic at the carbene carbon atom, while zerovalent Ru<sup>0</sup>=CF<sub>2</sub> species exhibit nucleophilic behavior. These observations demonstrate that the above classification of transition-metal carbene complex reactivity, according to position of the metal in the periodic table and the nature of the carbene substituent, is an oversimplification. The transition-metal methylene complexes reported in the literature exhibit reactivity ranging from electrophilic to nucleophilic, and these species are also important in demonstrating that the reactivity of metal-carbon double bonds represents a continuum rather than discrete classes.

At this point it is useful to define the terms "alkylidene", referring to complexes with H, alkyl, or aryl substituents on the carbon, and "carbene", referring to species with one or two heteroatom substituents.

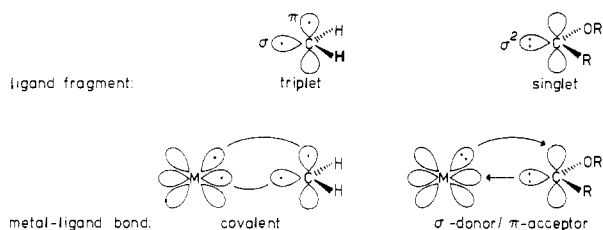
Two modes of multiple bonding are well recognized in chemistry. Covalent double bonds with  $\sigma$  and  $\pi$  components are familiar for the C=C bond of olefins. On the other hand, multiple bonding in metal carbonyl species is understood in terms of  $\sigma$  donation of a pair

of electrons on CO to an empty metal orbital, with  $\pi$  back-donation of a filled metal d orbital to an empty CO  $\pi^*$  orbital. The isolobal analogy, which allows replacement of an organic fragment by an ML<sub>n</sub> fragment of the appropriate symmetry,<sup>14</sup> suggests that multiple bonding between metal and carbon may be either donor/acceptor or covalent in nature.

The first indication that this would be a useful concept to apply to the bonding in metal carbene and alkylidene species originated in a theoretical study by Taylor and Hall.<sup>15</sup> They carried out a generalized molecular orbital calculation on a number of model carbene complexes which had close parallels to known species. When dissociation of the complexes into ground-state ML<sub>n</sub> and CR<sub>2</sub> fragments was calculated, two general cases appeared. The early-transition-metal alkylidene species gave triplet fragments, while the late-transition-metal carbene complexes gave singlet fragments. Intermediate cases (late metal alkylidenes or early metal carbenes) were calculated to have reduced bond strengths, reflecting the cost in energy of promoting one fragment to an excited state of the correct multiplicity.

This approach represents a valence bond rather than a molecular orbital picture of metal-carbene bonding. In the latter model, molecular orbitals are constructed from the appropriate orbitals of the metal and ligand components, and the electrons are then fed in to the resulting energy levels. Distinctions such as the ground-state configuration of the metal and ligand fragments are lost. In contrast, the valence-bond model takes each fragment in its ground-state configuration and overlaps orbitals of the correct electron occupancy and symmetry to form bonds. In this treatment, the distinction between covalent bonding by spin pairing of electrons in singly occupied orbitals and donor/acceptor bonding by overlap of doubly occupied with empty orbitals is apparent.

This approach was taken up by Carter and Goddard, who carried out generalized valence-bond calculations, with a high level of electron correlation, on a number of model carbene and alkylidene systems. The results of these extensive theoretical studies allowed the development of a unified prescription relating the nature of the bonding in metal-carbene systems to the metal,



**Figure 1.** Triplet and singlet metal and carbene fragments involved in covalent and donor/acceptor double bonds.

oxidation state, ancillary ligands, and carbene substituents. The following discussion is drawn from the conclusions of their studies.<sup>16-18</sup>

The metal and carbene fragments each have an orbital of  $\sigma$  symmetry and one of  $\pi$  symmetry. The relevant orbitals for the carbene fragment are the C  $sp^2$   $\sigma$  orbital and the C  $p\pi$  orbital. The metal has a  $\sigma$  orbital comprised of varying amounts of d and s character and a  $d\pi$  orbital. In a triplet fragment each of these orbitals is singly occupied, while a singlet fragment has one doubly occupied and one empty orbital (Figure 1). A covalent  $M=C$  bond is formed from triplet fragments by spin pairing of the C  $sp^2$   $\sigma$  with the metal  $\sigma$  electrons and the C  $p\pi$  and metal  $d\pi$  electrons, forming  $\sigma$  and  $\pi$  bonds, respectively. The donor/acceptor bond is comprised of singlet fragments: a  $\sigma$  bond from overlap of the doubly occupied C  $sp^2$   $\sigma$  orbital with the empty metal  $\sigma$  orbital, and a  $\pi$  back-bond formed by donation of the metal  $d\pi$  pair to the empty C  $p\pi$  orbital (Figure 1).

Thus factors that stabilize the metal and carbene fragments in the triplet state should give rise to a covalent, olefinic  $M=C$  bond, while metal and carbene fragments in singlet ground states will give donor/acceptor bonds. These factors are the nature of the metal (early or late; first-, second-, or third-row transition metal), the metal oxidation state, the ancillary ligands, and the carbene substituents. Some examples do fall into the simple categories proposed by the early workers in this field, while others involve a more complex interplay of factors with the result that there may not be much difference in energy between the two bonding modes. This will be the case for complexes with "mismatched" fragments; a singlet metal with a triplet carbene, or vice versa.

If the bonding type in  $L_nM=CXY$  systems can be rationalized, then this can be correlated with reactivity. For example, a covalent, olefinic-type  $M=C$  bond might be expected to exhibit nucleophilic reactivity at the carbene carbon, by analogy with the chemistry of olefins and similar unsaturated species. Reactivity of a donor/acceptor  $M=C$  bond will depend on the extent of, and balance between, the  $\sigma$ -donor and  $\pi$ -acceptor effects.

First, consider the carbene fragment CXY. If X and Y are  $\sigma$  donors but not  $\pi$  donors, then the C  $sp^2$   $\sigma$  orbital will be destabilized and the  $p\pi$  orbital stabilized. These effects will favor single occupation of both orbitals, forming a triplet  $\sigma\pi$  ground state. These criteria are fulfilled by H, alkyl and aryl substituents. In fact,  $CH_2$  has a triplet ground state, with the singlet excited state lying  $\sim 9$  kcal/mol higher in energy.<sup>19</sup>

On the other hand, electronegative substituents will lower the energy of the C  $sp^2$   $\sigma$  orbital by  $\sigma$  withdrawal. If the substituent is also a  $\pi$  donor, then the C  $p\pi$  or-

bita will be destabilized. Both these factors work to favor a singlet  $\sigma^2$  configuration for the ground state, with a doubly occupied C  $sp^2$   $\sigma$  orbital and an empty  $p\pi$  orbital. Free carbenes, CXY, where X and Y are  $NR_2$ , OR, F, or Cl are ground-state singlets. For example, the singlet state of  $CF_2$  is  $\sim 57$  kcal/mol lower than the triplet state.<sup>20-22</sup> Thus, examination of the carbene fragment alone suggests that replacing a  $CH_2$  by a  $CF_2$  ligand favors donor/acceptor over covalent bonding by  $\sim 66$  kcal/mol.

The discussion so far has established that alkylidene ( $CH_2$ , CHR,  $CR_2$ ) ligands have triplet ground states and favor covalent bonding. The first requirement of the metal for this mode of bonding is singly occupied orbitals. A low d electron count and ionic ancillary ligands will force the metal into a high spin state, with minimal spin pairing. A low d electron count is also important in minimizing the loss of exchange energy incurred as a result of spin pairing in bond formation. This will be true for the early transition metals, which readily form  $ML_n$  fragments containing charged ligands (Cp, Me, OR, etc.). Thus covalent  $M=C$  bonding is expected for early-transition-metal alkylidene species. An example is the complex  $Cp_2Ta(=CH_2)(CH_3)$ ,<sup>1</sup> which exhibits nucleophilic reactivity at the carbene carbon.

Heteroatom substituents on the carbene fragments stabilize the singlet ground state. Lone pairs on the metal suitable for  $\pi$  back-bonding are most likely when there is a high number of metal valence electrons, resulting in spin pairing. The presence of closed-shell ancillary ligands (CO,  $PPh_3$ ) will force the metal into a low-spin state with doubly occupied d orbitals in order to avoid repulsion from ligand electron pairs. Thus donor/acceptor  $M=C$  bonding is expected for low-valent or late-transition-metal complexes with carbene ligands (heteroatom substituents). Examples are the zerovalent pentacarbonyl group 6 alkoxy carbene complexes  $(CO)_5M(=C(OR)R)^2$  and the  $d^6$  ruthenium, osmium, and iridium dihalocarbene complexes  $MCl_2(CX_2)(CO)(PPh_3)_2$  (M, X = Ru, F; Ru, Cl; Os, Cl) and  $IrCl_3(=CCL_2)(PPh_3)_2$ .<sup>13,23-25</sup> All these complexes are electrophilic at the carbene carbon.

The situation for  $M=C$  bonding is not always as clear-cut as in the above examples. As mentioned in conjunction with the covalently bonded systems, exchange energy lost by spin pairing of metal with CXY electrons is a direct cost to the strength of the  $M=C$  bond. Exchange energy loss is not significant for donor/acceptor bonding since the d electrons are already paired in the  $ML_n$  fragment. Furthermore, the energy required to promote either the metal or the CXY fragment to a configuration suitable for either covalent or donor/acceptor bonding is another cost to the  $M=C$  bond strength. Exchange energy terms are higher for first than for second- or third-row metals. Thus moving down a column in the periodic table will introduce factors that may alter the balance between the two bonding modes. In addition, covalent or donor/acceptor bonding modes may both be accessible to one species when  $\pi$  back-bonding is possible but there is only an intermediate loss of exchange or promotional energy on forming a covalent bond.

These points are nicely illustrated by valence-bond calculations carried out for bonding in  $RuCH_2^+$  and  $FeCH_2^+$ .<sup>17,18</sup> Binding of the triplet ground state of  $CH_2$



to ground state, high-spin  $d^7$   $Ru^+$  was calculated to yield a stable, covalently bonded alkylidene complex. However, bonding singlet  $CH_2$  to  $d^7$   $Ru^+$  results in no exchange energy loss, and a donor/acceptor methylene complex was calculated to lie only  $\sim 12$  kcal/mol higher in energy than the covalently bonded complex.<sup>17</sup> However, this order is expected to be reversed for  $FeCH_2^+$  where the higher exchange energy loss incurred by forming a covalent bond to a first-row metal results in the donor/acceptor bond being favored.<sup>18</sup> These results are supported experimentally by the preparation of an electrophilic, donor/acceptor-type iron methylene complex,  $[CpFe(=CH_2)dppe]^+$ ,<sup>26</sup> and nucleophilic, alkylidene-type zerovalent ruthenium and osmium  $CH_2$  complexes  $MCl(NO)(=CH_2)(PPh_3)_2$ .<sup>6,11</sup> In contrast, the cationic  $d^6$  iridium methylene complex  $[IrBr(Me)(=CH_2)(PMe_3)_3]^+$  is so electrophilic that it can only be isolated as the pyridine adduct.<sup>27</sup>

The metal oxidation state is also important in determining reactivity. The covalent and donor/acceptor states calculated for  $RuCH_2^+$  can be considered as models for the zerovalent ruthenium and osmium complexes  $MCl(NO)(=CH_2)(PPh_3)_2$  and  $MCl(NO)(=CF_2)(PPh_3)_2$ . The  $CH_2$  species are expected to contain a covalent  $M=C$  bond, and this is supported by the observed nucleophilic reactivity. The singlet ground state of the  $CF_2$  fragment is favored by  $\sim 57$  kcal/mol, and thus the difluorocarbene complexes are expected to contain donor/acceptor  $M=C$  bonds, but for these complexes the experimentally observed reactivity is also nucleophilic. This is in sharp contrast to  $Ru(II)$  and  $Os(II)$  dihalocarbene complexes which contain donor/acceptor bonds but are, as expected, electrophilic in character. The explanation derives from the fact that  $\pi$  back-bonding from the zerovalent metal center is sufficiently effective to satisfy the electrophilic nature of the carbene carbon. The zerovalent osmium methylene and difluorocarbene complexes have both been structurally characterized, and the results will be compared in the next section.

Saturation of the metal center also figures in determining bond type. Ion beam studies demonstrated that  $MnCH_2^+$  undergoes olefin metathesis reactions, in contrast to the saturated species  $(CO)_5MnCH_2^+$  which will cyclopropanate olefins.<sup>28</sup> The former, unsaturated complex forms a covalent alkylidene bond between  $CH_2$  and high-spin,  $s^1d^5$   $Mn^+$  which has no lone pairs available for  $\pi$  back-bonding. The presence of five carbonyl ligands in the saturated complex results in a low-spin  $d^6$   $Mn(CO)_5$  fragment with lone pairs available for donor/acceptor bonding.<sup>18</sup> Again, this example illustrates the subtle balance between the factors affecting bond type and the corresponding chemical reactivity.

It is important to consider bond strengths of both covalent and donor/acceptor  $M=C$  bonds. Bond strengths calculated for both the covalent ground state and the low-lying donor/acceptor excited state of  $RuCH_2^+$  were found to be comparable: 68.0 and 65.8 kcal/mol, respectively.<sup>17</sup> The bond strengths for comparable saturated Ru complexes were estimated to be 85.5 kcal/mol for the covalent  $M=C$  bond and 65.8 for the donor/acceptor bond. Covalent bond formation to the saturated complex results in less exchange energy loss than bond formation to the unsaturated species,

thus increasing the bond strength. Exchange energy loss does not figure for a donor/acceptor bond to either complex. These results indicate that sufficiently strong  $M=C$  bonds for good chemical stability should be accessible through either covalent or donor/acceptor bonding mechanisms.

The energy requirement for promoting the carbene fragment to an excited state suitable for bond formation is a direct cost to the bond strength. This is illustrated by ion beam studies on  $NiCH_2^+$  and  $NiCF_2^+$ , which demonstrated that the  $Ni-C$  bond strength of the former is approximately 40 kcal/mol stronger than the latter.<sup>29</sup> This bond energy difference is similar to the singlet/triplet gap for free  $CF_2$ . Similarly, the  $C=C$  bond of  $CH_2=CH_2$  is calculated to be approximately 100 kcal/mol higher than that in  $CF_2=CF_2$ .<sup>30</sup>

Particularly strong covalent metal-carbon  $\pi$  bonds are expected for the heavier early transition metals as a result of effective overlap of the large d orbitals. In fact these metals figure in most of the examples of terminal metal alkylidene complexes. Contraction of d orbitals across a row means that weaker covalent metal-carbon  $\pi$  bonds are expected for the later transition metals, favoring bridging alkylidene complexes with two covalent single bonds over  $\sigma, \pi$ -bonded terminal alkylidene complexes for the later transition metals. Again, this prediction is borne out by experimental fact, with relatively few terminal alkylidene complexes known for the later metals, in contrast to the wide range and rich chemistry displayed by the bridging methylene and alkylidene complexes of groups 7-9.<sup>5,8</sup> On the other hand, formation of a bridging  $CF_2$  species would first require promotion of the singlet carbene to the triplet state with two unpaired electrons required to form two covalent single bonds. This results in a direct cost to the bond strength of approximately 57 kcal/mol and rationalizes why so few bridging mono- or dihalocarbene complexes are known. Monohalocarbenes where the other substituent is H or alkyl will bridge two metal centers easier than dihalocarbenes, since the singlet-triplet gap is smaller.<sup>21</sup>

The above discussion has been general for both metal carbene and alkylidene chemistry. It is appropriate now to summarize the results with special attention to dihalocarbene complexes. Both the methylene and dihalocarbene complexes of the second- and third-row group 8-10 metals are significant in that chemical reactivity spans the range from electrophilic to nucleophilic. Both covalent and donor/acceptor bonding is available to methylene complexes as a result of the small singlet/triplet energy gap in free methylene. The nature of the  $ML_n$  fragment often determines bond type in these cases. The much larger splitting of the states in free dihalocarbenes appears to constrain the bonding to the donor/acceptor type appropriate to the singlet ground state of the dihalocarbene fragment.

The early transition metals are most suited to covalent bonding because the lack of doubly occupied d orbitals in the ground state precludes  $\pi$  back-bonding, and the low number of valence d electrons results in only small promotional or exchange energy losses. The conclusion that dihalocarbene ligands are apparently constrained to donor/acceptor bonding rationalizes the lack of dihalocarbene complexes of the early transition metals. Monohalocarbene species with a zerovalent

chromium center are known, a few very reactive manganese difluorocarbenes have been observed spectroscopically, and it is not until the iron triad that isolable dihalocarbene species can be achieved. In this context, however, it must be noted that the early-transition-metal haloalkyl complexes which might be expected to be precursors to halocarbene species are also unknown. Although this bonding model rationalizes the current lack of early-transition-metal halocarbenes, this might also be a consequence of the lack of a suitable synthetic approach.

In contrast to the situation for early transition metals, low-valent, late transition metals are better suited for bonding to the singlet dihalocarbene fragment. The presence of doubly occupied d orbitals in group 8-10 and low-valent group 6 and 7 metal centers facilitates  $\pi$  back-bonding. Donor/acceptor bonding is also appropriate when the exchange or promotional energy cost for forming a covalent bond is too high, as when there is a high number of open-shell valence d electrons. The dihalocarbene ( $\text{CF}_2$ ,  $\text{CFCl}$ ,  $\text{CFBr}$ ,  $\text{CCl}_2$ ,  $\text{CBr}_2$ ) and monohalocarbene ( $\text{CXR}$ ,  $\text{C(X)NR}_2$ ,  $\text{C(X)OR}$ ,  $\text{C(X)SR}$ ) complexes of ruthenium, osmium and iridium are satisfactorily described by this bonding scheme.

A further strength of this bonding model is that although covalent bonding is seen to be compatible with nucleophilic reactivity, acceptance of donor/acceptor bonding for dihalocarbene complexes is still consistent with the observed reactivity, encompassing both nucleophilic and electrophilic reactions at the carbene carbon. The key to this is the extent to which  $\pi$  back-bonding to the strongly electron-withdrawing dihalocarbene ligand mediates the electrophilicity of the carbene carbon atom. Competition from Cp and CO ligands and the positive charge in  $[\text{CpFe(=CX}_2\text{)(CO)}_2]^+$  ( $\text{X} = \text{F, Cl}$ ) inhibits back-bonding to such an extent that these highly reactive, electrophilic species are at the limit of isolability.<sup>31,32</sup> On the other hand, the zerovalent metal center and electron-releasing  $\text{PPh}_3$  ligands in  $\text{MCl(NO)(=CF}_2\text{)(PPh}_3\text{)}_2$  ( $\text{M} = \text{Ru, Os}$ ) results in such effective  $\pi$  back-bonding that the electrophilicity of the carbene center is inhibited, and the complexes in fact display nucleophilic behavior.<sup>6,7,11</sup>

The consequences of the variation in electronegativity, polarizability, nucleophilicity, and electron donor/withdrawal properties on descending the elements of group 17 are well-known to organic and inorganic chemists alike. These factors continue to be significant in the context of the stability and reactivity of halocarbene complexes. Although examples of both  $\text{CF}_2$  and  $\text{CCl}_2$  metal complexes are well represented, the following discussion will reveal that only one example of a  $\text{CBr}_2$  complex is known, and a  $\text{Cl}_2$  complex is implicated only as a reaction intermediate.

### III. Synthesis

The bonding scheme discussed in the previous section for transition-metal dihalocarbene complexes indicates that a range of such species should be sufficiently stable to handle under laboratory conditions. The limitation lies in the availability of suitable synthetic routes to  $\text{L}_n\text{M=CX}_2$  species. Several methods have been developed, but each one is appropriate for only a limited number of transition-metal substrates. A notable feature of these synthetic schemes is the predominance of

metal trihalomethyl species as dihalocarbene precursors.

The chemistry of transition-metal  $\text{CF}_3$  species was the focus of much attention, and even some controversy, in organometallic chemistry in the 1960s and early 1970s. As a result, many trifluoromethyl complexes are known, and these offer the possibility of modification of the  $\text{CF}_3$  ligand to form  $\text{M=CX}_2$  complexes. This decade has seen further new  $\text{CF}_3$  complexes reported, some specifically tailored to be precursors to  $\text{M=CF}_2$  species. Alternatively, group 12 (Cd, Hg) trihalomethyl species are useful as reagents for transfer of  $\text{CX}_2$  or  $\text{CX}_3$  fragments to transition-metal substrates.

This important role played by transition-metal and group 12 trifluoromethyl complexes warrants a brief discussion of the synthesis, properties, and selected aspects of the chemical reactivity of these species. The preparative routes to terminal and bridging dihalocarbene and monohalocarbene complexes will be covered exhaustively.

#### A. Trihalomethyl Complexes

The transition-metal chemistry of halomethyl species is centered largely around fluoride as the halide element. The  $\text{CX}_3$  complexes of the heavier halides are much more reactive than their fluoride congeners, and correspondingly fewer examples are known. However there are a number of cases where they are implicated as intermediates in the formation of  $\text{M=CX}_2$  complexes. The more readily isolable  $\text{CF}_3$  species may serve as models for the behavior of their more reactive counterparts. In fact, one of the most useful routes to  $\text{CX}_3$  and  $\text{CX}_2$  complexes of the heavier halides is halide exchange of  $\text{M-CF}_3$  with boron trihalides.

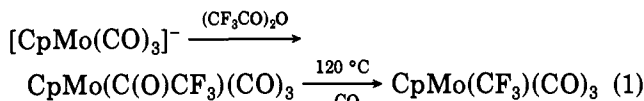
##### 1. Synthesis of Transition-Metal Trifluoromethyl Species

The synthesis of transition-metal trifluoromethyl complexes was reviewed during the early period of interest in this chemistry,<sup>33</sup> and a more recent review brings developments in the area up to date.<sup>34</sup> The synthetic methods developed in the 1960s fall mostly into two classes: decarbonylation of trifluoroacetyl complexes and oxidative addition of  $\text{CF}_3\text{I}$  to suitable metal substrates. These routes were necessarily restricted to the low-valent, electron-rich late-transition-metal complexes and have been used for introducing up to two  $\text{CF}_3$  groups per molecule. More recently, methods involving group 12 trifluoromethyl complexes as  $\text{CF}_3$  transfer reagents and sophisticated metal atom condensation techniques were developed.

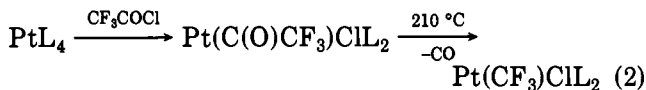
Once a  $\text{CF}_3$  group has been introduced into a complex, in general, new  $\text{CF}_3$  complexes can be produced by well-established routes such as ancillary ligand substitution or cation formation, and these will not be discussed here.

**a. Decarbonylation of Trifluoroacetyl Complexes.** Metal anion substitution of  $\text{CF}_3\text{COCl}$  or  $(\text{CF}_3\text{CO})_2\text{O}$  produces a metal trifluoroacetyl species,  $\text{L}_n\text{M-C(O)CF}_3$ , which can be thermally (or sometimes photolytically) decarbonylated to the trifluoromethyl complex  $\text{L}_n\text{M-CF}_3$ .<sup>34-37</sup> This technique, used to prepare  $\text{CF}_3$  complexes of Mo, Mn, Fe, Co, and Ir, is illustrated for a Mo example in eq 1.

Oxidative addition of  $\text{CF}_3\text{COCl}$  or  $(\text{CF}_3\text{CO})_2\text{O}$  to neutral, low-valent  $\text{L}_n\text{M}$  species ( $\text{Pt(O)}, \text{Ir(I)}$ ) is an al-



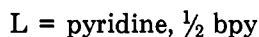
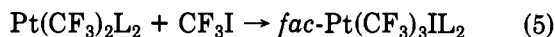
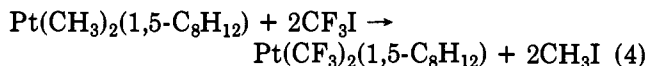
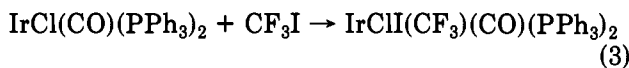
ternate route to trifluoroacetyl complexes, which can then be decarbonylated as above (eq 2).<sup>38,39</sup>



The high temperature used for the thermal decarbonylation steps demonstrates the good thermal stability of transition-metal  $\text{CF}_3$  complexes. The decarbonylation is presumed to proceed via  $\text{CF}_3$  migration to the metal, followed by CO loss. The reverse migration of  $\text{CF}_3$  from metal to CO has never been observed, although this process is extremely facile for the methyl analogues.<sup>35,40</sup>

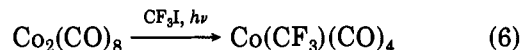
The decarbonylation method does have some limitations. For the anion route a low-valent metal capable of forming an anion is required. Very reactive anions like  $[\text{CpFe}(\text{CO})_2]^-$  can actually displace  $\text{F}^-$  from  $\text{M}-\text{C}(\text{O})\text{CF}_3$  species, resulting in reduced yields.<sup>35</sup> The decarbonylation step is promoted by the presence of strongly electron-withdrawing ancillary ligands like CO thus analogues substituted with  $\text{PPh}_3$  for CO may require much higher temperatures, resulting in complex decomposition. Decarbonylation is also difficult to achieve for second- and third-row transition-metal complexes which tend to have higher M-C bond strengths. Platinum and iridium are the only heavier elements for which this method has been successful.<sup>38,39</sup>

**b. Oxidative Addition of  $\text{CF}_3\text{I}$ .** Displacement of iodide from  $\text{RI}$  by an anionic species,  $[\text{ML}_n]^-$ , is not practical for  $\text{R} = \text{CF}_3$ , as the more electronegative  $\text{CF}_3$  group is displaced to give  $\text{ML}_n\text{I}$  as the product. However  $\text{CF}_3\text{I}$  will oxidatively add to coordinatively unsaturated low-valent  $d^8$  and  $d^{10}$  metal centers of the cobalt and nickel triads and gold (eq 3).<sup>34,39</sup> The reaction may also proceed via oxidative addition of  $\text{CF}_3\text{I}$  to metal alkyl precursors and subsequent elimination of  $\text{RR}$  or  $\text{RI}$  to give bis(trifluoromethyl) species. Note that elimination of the alkyl group is more favorable than elimination of the trifluoromethyl group (eq 4).<sup>41</sup> The only known transition-metal tris(trifluoromethyl) complex was made by oxidative addition of  $\text{CF}_3\text{I}$  (eq 5).<sup>42</sup>

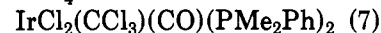


To date, the oxidative addition of  $\text{CF}_3\text{I}$  has been limited to even-electron ( $d^8$  or  $d^{10}$ ) rather than odd-electron ( $d^7$  or  $d^9$ ) metal substrates.

The use of  $\text{CF}_3\text{I}$  in oxidative processes other than simple two-electron oxidative addition also gives rise to  $\text{CF}_3$  complexes (eq 6).<sup>43</sup> However examples of such reactions are limited as  $\text{CF}_3\text{I}$  is a poor oxidizing agent (relative, for example, to  $\text{I}_2$ ).



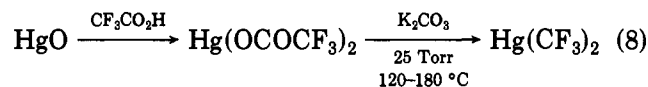
In a single example,  $\text{CCl}_4$  serves as the source of the relatively rare  $\text{CCl}_3$  ligand, by oxidative addition to an Ir(I) complex (eq 7).<sup>44</sup> A trichloromethyl intermediate  $\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2 + \text{CCl}_4 \rightarrow$



may also be involved in the reaction of a reduced iron porphyrin species with  $\text{CCl}_4$  to produce a dichlorocarbene complex,<sup>45</sup> as discussed in section III.B.5.

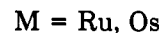
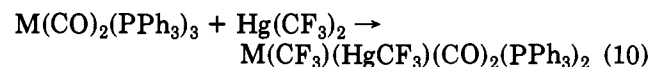
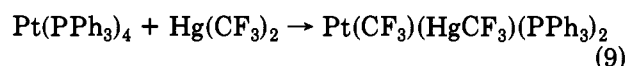
**c. Activated Metal Species with  $\text{CF}_3$  Radicals.** The activation of either the metal substrate or the trifluoromethyl fragment by an external energy source has led to a number of new trifluoromethyl complexes. These have been summarized in a recent review of metal trifluoromethyl chemistry.<sup>34</sup> Metal atom condensation with  $\text{CF}_3\text{I}$  gives the highly reactive species  $\text{CF}_3\text{MI}$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Ag}, \text{Zn}$ ), and ultrasound activation has been used to prepare  $\text{CF}_3\text{ZnI}$ . Reaction of metal halides with  $\text{CF}_3$  radicals produced by radio-frequency discharge has produced  $\text{M}(\text{CF}_3)_2(\text{PMe}_3)_2$  ( $\text{M} = \text{Ni}, \text{Pd}$ ). Zinc and cadmium trifluoromethyl species have been achieved by electrochemical oxidation in the presence of  $\text{CF}_3\text{I}$ . Although novel, however, these specialized techniques are not accessible to most synthetic laboratories, and the reaction products are often highly reactive.<sup>34</sup>

**d.  $\text{CF}_3$  Transfer from Group 12 Metals.** Although trifluoromethyl mercurials were the first metal complexes containing the  $\text{CF}_3$  ligand to be prepared,<sup>46</sup> they were not utilized as a source of the  $\text{CF}_3$  ligand until this decade. The extremely thermally robust complex  $\text{Hg}(\text{CF}_3)_2$  is prepared by decarboxylation of mercuric bis(trifluoroacetate) and can be conveniently purified by sublimation (eq 8).<sup>47,48</sup>

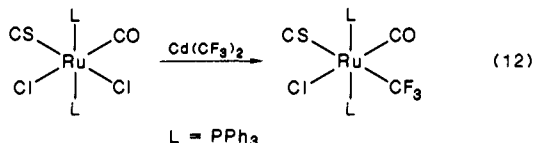
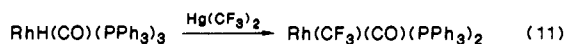


When  $\text{Hg}(\text{CF}_3)_2$  is treated with  $\text{Cd}(\text{Me})_2$  in glyme (1,2-dimethoxyethane),  $\text{Cd}(\text{CF}_3)_2$  is formed as one component of an equilibrium mixture of all possible transmetalation products. This highly reactive cadmium species is isolated as the glyme adduct, after the other more volatile products are removed at low pressure. Facile base exchange gives adducts of the general form  $\text{Cd}(\text{CF}_3)_2\text{-base}$ . Stronger bases like pyridine render the cadmium species more stable but less reactive, while weaker bases like THF have the opposite effect. The glyme adduct  $\text{Cd}(\text{CF}_3)_2\text{-glyme}$  offers the best compromise between reactivity and stability.<sup>48-50</sup>

The mercurial  $\text{Hg}(\text{CF}_3)_2$  oxidatively adds across one  $\text{Hg}-\text{C}$  bond to some low-valent metal substrates, producing novel complexes containing both  $\text{CF}_3$  and  $\text{Hg}(\text{CF}_3)$  ligands (eq 9).<sup>51</sup> In the group 8 example shown in eq 10 the yield is good for ruthenium but poor for osmium.<sup>23</sup> The chemistry of the ruthenium complex is important in opening up a route to new  $\text{M}=\text{CX}_2$  complexes and will be described below.



The mercury complex is effective for transfer of one or more  $\text{CF}_3$  groups to several main-group-metal halides (Ge, Sn, P, Sb, Bi), producing species such as  $\text{Sn}(\text{CF}_3)_2\text{Br}_2$  from  $\text{SnBr}_4$ .<sup>47</sup> The cadmium complex is even more reactive, giving  $\text{Sn}(\text{CF}_3)_4$  from the same substrate. Both the mercury and cadmium reagents will transfer  $\text{CF}_3$  to suitable transition-metal species. Rh(I) and Ir(I) hydride complexes react with the mercury reagent (eq 11),<sup>37,52</sup> and the cadmium complex is effective for the preparation of  $\text{CpCo}(\text{CO})_2(\text{CF}_3)$  and  $\text{M}(\text{CF}_3)\text{Br}(\text{PET}_3)_2$  ( $\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$ ) from  $\text{CpCo}(\text{CO})_2\text{I}$  and  $\text{MBr}_2(\text{PET}_3)_2$ , respectively.<sup>53,54</sup> In the example in eq 12, the strongly trans-labilizing CS ligand directs the regioselectivity of the reaction.<sup>55</sup>



Other trihalomercurials are important as sources of dihalocarbenes. A series of phenylmercury derivatives,  $\text{PhHg}(\text{CX}_3)$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ), are useful for the transfer of a dihalocarbene fragment,  $\text{CX}_2$ , to organic substrates. Mechanistic studies concluded that decomposition of the mercurial generates free carbenes which are then trapped by the substrate.<sup>56</sup> However, there has been no substantiated report of capture of a free carbene by metal substrates. Attempts to use  $\text{PhHg}(\text{CX}_3)$  as reagents for the preparation of metal  $\text{CX}_3$  or  $\text{CX}_2$  species were unsuccessful, with transfer of the phenyl group instead of the halocarbon fragment being observed in some cases.<sup>57</sup> In contrast, the reagent  $\text{Hg}(\text{C-Cl}_3)_2$  has been useful as a source of the dichlorocarbene ligand. This reagent is produced as shown in eq 13.<sup>58</sup>

$$2\text{CCl}_3\text{CO}_2\text{Na} + \text{HgCl}_2 \rightarrow \text{Hg}(\text{CCl}_3)_2 + 2\text{NaCl} + 2\text{CO}_2 \quad (13)$$

## 2. Properties of Transition-Metal Trifluoromethyl Complexes

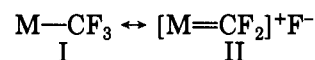
Transition-metal  $\text{CF}_3$  complexes exhibit properties markedly different than their alkyl counterparts. The much greater thermal stability of the  $\text{CF}_3$  species is exemplified by the preparative reactions involving thermolysis at temperatures up to 210 °C.<sup>33,38,59</sup> Structural studies indicate very strong M–C bonds but rather weak C–F bonds. The M–C bonds are on average 0.05 Å shorter for M– $\text{CF}_3$  than M–alkyl species.<sup>38,60,61</sup> The C–F bonds are longer, and the C–F stretching frequencies ( $\nu(\text{C–F})$ ) approximately 100  $\text{cm}^{-1}$  lower, than those observed for other species ( $\text{CF}_3\text{I}$  or  $\text{L}_n\text{M–C}(\text{O})\text{CF}_3$ ) containing  $\text{sp}^3$  C–F bonds.<sup>35,62–64</sup> Finally, a large shift to lower field is observed in the  $^{19}\text{F}$  NMR spectrum of  $\text{L}_n\text{M–CF}_3$  relative to  $\text{L}_n\text{M–C}(\text{O})\text{CF}_3$  complexes.<sup>65</sup> However, the NMR trans influence of  $\text{CF}_3$  and  $\text{CH}_3$  ligands is comparable, and the structural trans influence of the  $\text{CF}_3$  ligand is actually less than that of  $\text{CH}_3$ .<sup>38</sup> Chemically, the fluorine substituents on  $\text{C}_\alpha$  of transition-metal perfluoroalkyl complexes are much more reactive than those on the  $\text{C}_\beta$  or  $\text{C}_\gamma$  positions, consistent with the longer  $\text{C}_\alpha\text{–F}$  bond lengths. Examples of this enhanced reactivity will be apparent below.

The X-ray crystal structure of the ruthenium complex  $\text{Ru}(\text{CF}_3)(\text{HgCF}_3)(\text{CO})_2(\text{PPh}_3)_2$  provides an excellent

example of structural differences, within the same molecule, between  $\text{CF}_3$  groups bonded to a transition metal and a main-group metal.<sup>23</sup> The Ru– $\text{CF}_3$  and Hg– $\text{CF}_3$  distances of 2.08 (1) and 2.17 (1) Å and the average RuC–F and HgC–F distances of 1.38 (1) and 1.29 (1) Å, respectively, illustrate the shorter M–C and longer C–F bond lengths of the transition-metal-bonded  $\text{CF}_3$  ligand. The Ru– $\text{CF}_3$  bond is only slightly longer than the Ru–CO bond (2.04 (2) Å) trans to the  $\text{CF}_3$  group and is approximately 0.14 Å shorter than a typical Ru–C( $\text{sp}^3$ ) single bond.<sup>66</sup> In a second example, isostructural complexes  $\text{PtClR}(\text{PMe}_2\text{Ph})_2$  ( $\text{R} = \text{CF}_2\text{CF}_3, \text{CH}_3$ ) exhibit respective Pt–C bond lengths of 2.00 (1) and 2.08 (1) Å, again illustrating the comparison between alkyl and fluoroalkyl ligands.<sup>38</sup>

## 3. Bonding in Transition-Metal Trifluoromethyl Complexes

Attempts to rationalize the relatively strong M–C and weak C–F bonds of  $\text{CF}_3$  complexes, evidenced by short M–C and long C–F bond lengths and low values of  $\nu(\text{CF})$ , sparked off a considerable controversy concerning the bonding in transition-metal  $\text{CF}_3$  complexes. An early suggestion was that the electronegative  $\text{CF}_3$  group causes contraction of the metal d orbitals, resulting in a strengthened M– $\text{CF}_3$  bond.<sup>61</sup> Another proposal was a hyperconjugation argument that invoked “no-bond” resonance structures like II.<sup>35</sup>

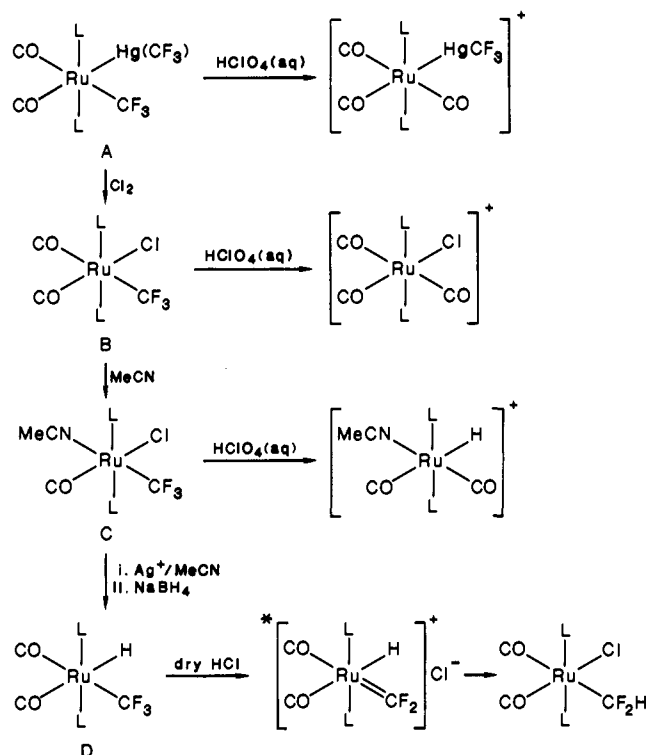


The most controversial proposal was that replacement of an H substituent of an alkyl group by the F of a  $\text{CF}_3$  group lowered the energy of the antibonding C–F  $\sigma^*$  orbital sufficiently that it could act as a metal  $d\pi$  acceptor orbital. The resulting  $\pi$  back-bonding would impart some double-bond character to the M–C bond and would be consistent with the shorter M–C and longer C–F bonds.<sup>35,62,63,67</sup>

This proposal has been disputed, however.<sup>38,68,69</sup> A force constant analysis on  $\nu(\text{CO})$  was carried out for a large series of complexes,  $\text{RMn}(\text{CO})_5$ , where R included  $\text{CH}_3, \text{CF}_3$ , alkyl, perfluoroalkyl, aryl, halide, and main group alkyl ligands.<sup>68</sup> The  $\sigma$  and  $\pi$  effects were separated, allowing differentiation between electron withdrawal by inductive ( $\sigma$ ) or back-bonding ( $\pi$ ) mechanisms for each ligand. The  $\text{CH}_3$  and  $\text{CF}_3$  ligands were found to be equally poor  $\pi$ -electron acceptors, suggesting that  $\text{CF}_3$  is a strongly  $\sigma$ -withdrawing but not a  $\pi$ -withdrawing ligand. Intuitive reasoning based on the synergic nature of metal–ligand bonding suggests that the polarity of the M– $\text{CF}_3$   $\sigma$  bond would diminish the tendency for  $\pi$  bonding of the same polarity.<sup>68</sup>

The results of this study were supported by a qualitative electrostatic argument also based on  $\sigma$ -bonding effects. The electronegativity of the  $\text{CF}_3$  group will increase the s character of the C  $\sigma$  orbital and will induce a higher positive charge on the metal, leading to contraction of the metal  $\sigma$  orbitals. Both effects will improve overlap between the metal and carbon  $\sigma$  orbitals, resulting in a stronger bond.<sup>61,69</sup> This proposal is supported by photoelectron spectroscopic studies on  $\text{RMn}(\text{CO})_5$  ( $\text{R} = \text{CH}_3, \text{CF}_3$ ) and Fenske–Hall calculations on the same compounds<sup>69,70</sup> in which the s character of the C–F or C–H and the Mn–C bonds was



SCHEME I<sup>a</sup>

<sup>a</sup>L = PPh<sub>3</sub>; the asterisk (\*) = the intermediate, not isolated.

analyzed. The experimental observations could be explained without invoking  $\pi$  back-bonding. The C-F bonds of CF<sub>3</sub> use C orbitals with more p character than do the C-H bonds of CH<sub>3</sub>; thus the C orbital (6a<sub>1</sub>) involved in  $\sigma$  bonding to the metal has correspondingly more s character for M-CF<sub>3</sub>. The bonding electrons are held closer to the C atom leading to a shorter M-C bond. This also explains the longer C-F bonds since the 6a<sub>1</sub> M-C bonding orbital, which is actually antibonding in the C-F region, has a higher occupancy for Mn(CO)<sub>5</sub>(CF<sub>3</sub>) than does the corresponding orbital in ICF<sub>3</sub>, resulting in longer C-F bonds in the former species. A further electrostatic effect,  $\sigma$ -electron withdrawal by the fluorine substituents, results in a more positively charged carbon center in CF<sub>3</sub> than in CH<sub>3</sub>. This positive charge stabilizes the metal orbitals such that there is stronger bonding to all ligands in metal trifluoromethyl complexes.<sup>69</sup>

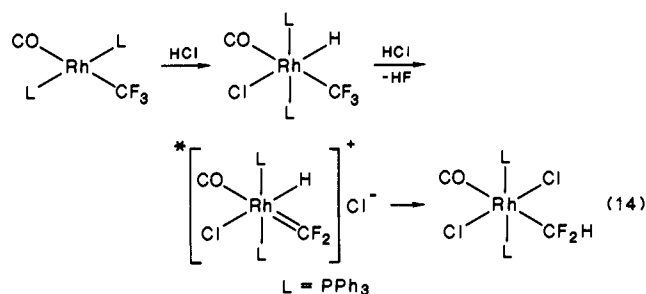
These more sophisticated arguments do seem to better account for the observed properties of transition-metal CF<sub>3</sub> complexes than do the qualitative proposals of  $\pi$  back-bonding effects. However, one reservation is that both the above studies focused on Mn(CO)<sub>5</sub>R complexes.<sup>68,69</sup> The Mn(CO)<sub>5</sub> fragment is a poor choice for a study to probe the existence of  $\pi$  back-bonding, which would be most difficult to observe in the presence of five competing carbonyl ligands.

4. Reactivity of the CF<sub>3</sub> Ligand toward Acids

The shorter M-C and longer C-F bonds found for M-CF<sub>3</sub> complexes translate, in chemical reactivity terms, into enhanced lability of the fluorine substituents while retaining the M-C bond intact. This is the essence of the utility of M-CF<sub>3</sub> species as precursors to M=CF<sub>2</sub> complexes. Selective removal of a single F would transform a CF<sub>3</sub> fragment into a CF<sub>2</sub> ligand.

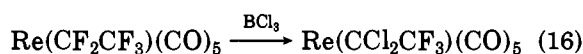
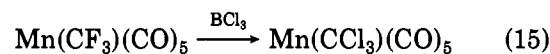
Exchange of the fluoride substituents of a coordinated CF<sub>3</sub> group for heavier halide elements would result in a chemically reactive CX<sub>3</sub> ligand, which may provide a route to other CX<sub>2</sub> ligands. Both these possibilities can be explored by examining the susceptibility of the CF<sub>3</sub> ligand toward electrophilic attack by both protic and Lewis acids.

**a. Protic Acids.** The ruthenium CF<sub>3</sub> complex A shown in Scheme I forms derivatives B and C by halogen-induced cleavage of the Ru-Hg bond and subsequent substitution of the labile CO ligand trans to the CF<sub>3</sub> ligand.<sup>23</sup> All three complexes react with protic acids resulting in hydrolysis of the CF<sub>3</sub> ligand. The product of hydrolysis of A retains the CF<sub>3</sub> group bound to Hg intact, again illustrating the very different reactivity of CF<sub>3</sub> bound to a transition metal. The reaction of the hydride derivative D with HCl to give a CF<sub>2</sub>H complex suggests that difluorocarbene intermediates may be involved in the hydrolysis reactions.<sup>55</sup> Similar reactivity is observed for the rhodium complex Rh(CF<sub>3</sub>)(CO)-(PPh<sub>3</sub>)<sub>2</sub> which reacts with HCl to give a CF<sub>2</sub>H species (eq 14).<sup>52</sup>

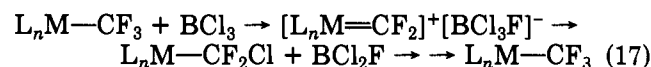


A plausible mechanism involving abstraction of a labile F<sup>-</sup> to form an intermediate CF<sub>2</sub> species can be proposed for all the reactions in Scheme I and eq 14. In each case H<sup>+</sup> abstraction of F<sup>-</sup> leads to loss of HF and formation of a very electrophilic cationic difluorocarbene intermediate. Rapid hydrolysis by nucleophilic attack at the carbene carbon leads to a CO ligand, except for the reactions of derivative D or the Rh complex where intramolecular migration of the hydride to form a CF<sub>2</sub>H ligand competes favorably with hydrolysis.

**b. Lewis Acids.** In a number of examples, the electrophilic boron trihalides BCl<sub>3</sub>, BBr<sub>3</sub>, and BI<sub>3</sub> attack the coordinated CF<sub>3</sub> ligand resulting in exchange of fluorine to give a new trihalomethyl complex (eq 15).<sup>71,72</sup> The new CCl<sub>3</sub> complex exhibits a  $\nu$ (CCl) stretch lower than that of RCCl<sub>3</sub> (R = alkyl), indicating that some C-X bond weakening may occur for CCl<sub>3</sub> coordinated to a transition metal. This exchange is specific for fluorines on the carbon  $\alpha$  to the metal, as shown in eq 16.<sup>71,72</sup>



Although the mechanism of halide exchange is not known, a stepwise process involving cationic intermediate M=CX<sub>2</sub><sup>+</sup> species with BX<sub>4</sub><sup>-</sup> counterions is possible (eq 17). An alternative mechanism would be a concerted, four-centered exchange.<sup>71,72</sup>

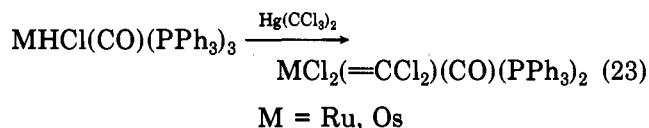




cussed in detail in section V.B.

### 3. Dichlorocarbene Complexes Derived from $Hg(CCl_2)_2$

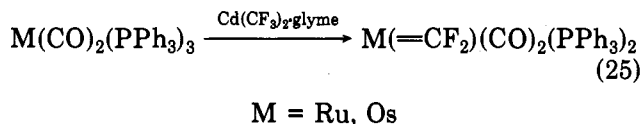
The use of  $Hg(CF_3)_2$  in transferring a  $CF_3$  group to a suitable metal substrate was described earlier. The trichloromethyl analogue is presumably also effective for the same process, but the more reactive  $M-CCl_3$  intermediate is not observed, instead losing chloride to form the dichlorocarbene complex  $M=CCl_2$ . Ru, Os, and Ir  $d^6$  hydrido tris(triphenylphosphine) complexes are suitable substrates, providing a one-step route to  $d^6$  dichlorocarbene complexes (eq 23 and 24).<sup>13,24,25</sup> Loss of a phosphine ligand and deposition of elemental mercury is observed for each reaction.



The Os and Ir complexes were structurally characterized, the latter example being the first X-ray structure of a dihalocarbene without disorder problems.<sup>25</sup> All the complexes are electrophilic at the carbene carbon, displaying a rich chemistry when treated with a wide variety of nucleophiles. These reactions will be discussed in depth in section V.

### 4. Difluorocarbene Complexes Derived from $Cd(CF_3)_2 \cdot Glyme$

The mercurial  $Hg(CF_3)_2$  oxidatively added, across the  $Hg-C$  bond, to  $Ru(CO)_2(PPh_3)_3$  yielding  $Ru(CF_3)(HgCF_3)(CO)_2(PPh_3)_2$ . A derivative of this complex is the  $d^6$  Ru(II) difluorocarbene complex  $RuCl_2(=CF_2)(CO)(PPh_3)_2$ , discussed in section III.A.<sup>23</sup> In contrast, when the more reactive reagent  $Cd(CF_3)_2 \cdot glyme$  is used with zerovalent Ru and Os substrates, the result is a net direct transfer of the  $CF_2$  fragment with no oxidation state change at the metal (eq 25).<sup>6,7,76</sup>



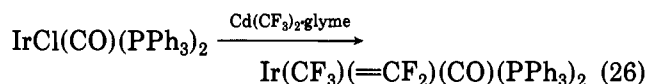
Other zerovalent precursors,  $RuCl(NO)(PPh_3)_2$ ,  $OsCl(NO)(PPh_3)_3$ , and  $Os(CO)(CS)(PPh_3)_3$ , react similarly, giving  $MCl(NO)(=CF_2)(PPh_3)_2$  (M = Ru, Os) and  $Os(=CF_2)(CO)(CS)(PPh_3)_2$ , respectively. The Os nitrosyl complex was the subject of an X-ray crystal structure determination.<sup>6,7</sup>

All the products are formally  $d^8$  zerovalent  $M=CF_2$  species and are much less moisture sensitive than the  $d^6$  Ru(II)  $CF_2$  and Ru(II) and Os(II)  $CCl_2$  complexes discussed above, indicating that their chemical reactivity is much less electrophilic in nature than the divalent metal species. The zerovalent complexes in fact display nucleophilic behavior.<sup>6,7,76</sup>

The versatility of the group 12 trifluoromethyl reagents is well demonstrated by the preparation of difluorocarbene complexes containing the same metal in two different oxidation states: Ru(II) and Ru(0) complexes are produced via the Hg and Cd reagents, respectively, and the resulting difluorocarbene species

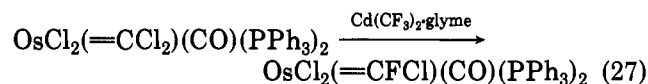
display reactivity ranging from electrophilic to nucleophilic. This is an important observation in transition-metal dihalocarbene chemistry and one that contributes to our understanding of metal carbene chemistry in general. The rationalization of this chemistry from a bonding point of view was discussed previously; the reactivity of these complexes will be examined in depth in section V.C.

The cadmium complex is also effective for  $CF_2$  transfer to  $d^8$  iridium centers.<sup>37</sup> A room-temperature reaction of  $Cd(CF_3)_2 \cdot glyme$  with  $IrI(CO)(PPh_3)_2$  gives  $IrI(=CF_2)(CO)(PPh_3)_2$ . At higher temperatures, reaction of the cadmium species with Vaska's complex or with  $Ir(CF_3)(CO)(PPh_3)_2$  results in transfer of  $CF_2$  to the Ir center and also, for the former substrate, replacement of chloride with  $CF_3$  (eq 26).<sup>37</sup> Other ex-



amples of  $CF_3$  transfer to transition-metal substrates were mentioned above.<sup>34</sup> This is the only example where both  $CF_3$  and  $CF_2$  are transferred from Cd to a single metal center. Attempts to prepare rhodium  $CF_2$  complexes by reaction of  $Cd(CF_3)_2 \cdot glyme$  with  $RhCl(PPh_3)_3$  were unsuccessful, giving  $RhCl(CO)(PPh_3)_2$  as the product.<sup>52</sup>

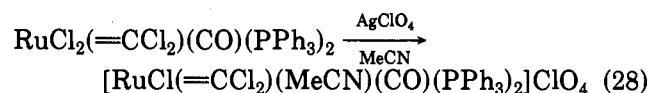
One further reaction of involving  $Cd(CF_3)_2 \cdot glyme$  is exchange of a chloro for a fluoro substituent in a metal  $CCl_2$  complex, yielding a  $CFCl$  species (eq 27).<sup>77</sup> An



analogy for this reaction is the conversion of  $RC(=O)Br$  to  $RC(=O)F$  upon reaction with  $Cd(CF_3)_2 \cdot glyme$ .<sup>50</sup> If an  $M=CCl_2$  species is considered to be an acyl halide analogue, then the reaction of the osmium  $CCl_2$  complex is an example of similar reactivity.

### 5. Modification of the Coordination Sphere

Some  $d^6$ , Ru(II) and Os(II) dihalocarbene complexes are subject to  $Ag^+$ -mediated abstraction of the chloride ligand *trans* to the carbene ligand. Coordination of acetonitrile produces new, cationic dihalocarbene complexes. The reaction is shown in eq 28 for a ruthenium

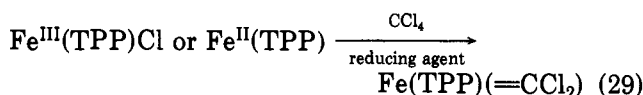


example, and the other reactions are summarized in section V.D and in Table X.<sup>57,77,78</sup> The reaction is only successful for complexes containing  $CCl_2$  and  $CFCl$  ligands; cationic  $CF_2$  species are very electrophilic and are not isolable. Cationic  $CCl_2$  complexes with more electron-withdrawing ligands are also very reactive (section V).

### 6. Metalloporphyrin Dihalocarbene Complexes

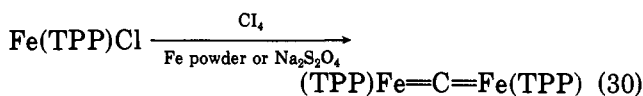
The iron tetraphenylporphyrin complex,  $Fe^{II}(TPP)$ , when treated with carbon tetrachloride in benzene, forms  $Fe^{III}(TPP)Cl$ . When the same reaction was carried out in the presence of a reducing agent (sodium dithionite,  $H_2/Pd$ , or iron powder), the product was the first transition-metal dihalocarbene complex and the first metalloporphyrin carbene species to be isolated (eq

29).<sup>10</sup> Two reducing equivalents are required in the transformation of Fe<sup>III</sup>(TPP)Cl to the product.

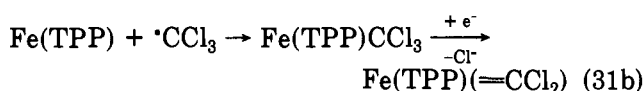
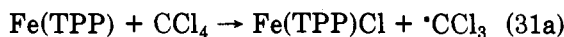


The dichlorocarbene complex is a diamagnetic, low-spin iron(II) species. The five-coordinate complex can bind a sixth ligand (pyridine, MeOH, THF, *N*-methylimidazole) in the vacant axial coordination site.<sup>10</sup> An X-ray crystal structure of Fe(TPP)(=CCl<sub>2</sub>)(OH<sub>2</sub>) confirms the carbene formulation.<sup>79</sup> In the presence of excess pyridine, Fe(TPP)(py)<sub>2</sub> is slowly formed, perhaps via nucleophilic attack at the carbene ligand. Electrophilic behavior at the carbene carbon is a characteristic of these d<sup>6</sup> complexes. The electron-rich porphyrin ligand may be important in stabilizing the dihalocarbene ligand.

A variety of dihalocarbene complexes was produced in the same manner as the dichlorocarbene complex, with carbene fragments CBr<sub>2</sub>, CF<sub>2</sub>, CFCl, and CFBBr being derived from the respective halomethyl species CBr<sub>4</sub>, CF<sub>2</sub>Br<sub>2</sub>, CFCF<sub>3</sub>, and CFBBr<sub>3</sub>.<sup>45</sup> The dibromocarbene complex, the only example of an M=CBr<sub>2</sub> species to be isolated and fully characterized, is more reactive toward nucleophiles than the chloro-substituted congener. The iodicarbene analogue is so reactive that it cannot be isolated but is presumed to be the intermediate in the formation of the novel μ-carbido complex (TPP)Fe=C=Fe(TPP) (eq 30).<sup>80</sup>



The mechanism of formation of the dihalocarbenes has not been investigated but was proposed to occur via initial formation of a trihalomethyl radical (eq 31a), which may then form an iron σ-alkyl intermediate (eq 31b). Reaction of substrates CXR<sub>3</sub>, containing only one



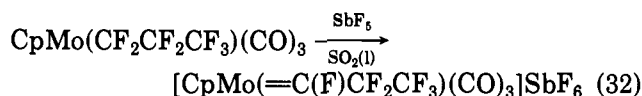
C-X bond, with iron porphyrins under reducing conditions gave stable iron(III) σ-alkyl complexes, supporting this proposal. Reduction of the intermediate (TPP)FeCCl<sub>3</sub> complex may lead to loss of a Cl substituent, forming the dichlorocarbene product.<sup>45</sup> Reduced iron species may also be involved. Production of ruthenium porphyrin alkylidene species from reaction of a zerovalent, anionic complex, [Ru(TTP)]<sup>2-</sup>, with geminal dihaloalkanes may be a model for the iron reaction.<sup>81</sup>

## C. Monohalocarbene Complexes

### 1. Metal Haloalkyl Precursors

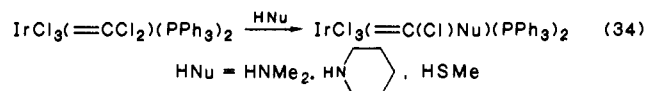
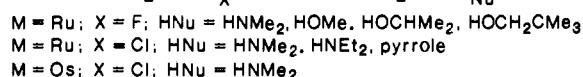
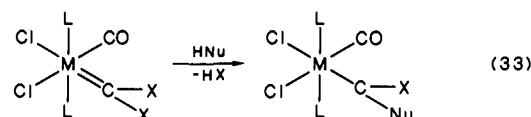
The fluoride exchange using BX<sub>3</sub> reagents or SbF<sub>5</sub>-mediated fluoride abstraction reactions discussed for M-CF<sub>3</sub> complexes are general for higher fluoroalkyl complexes, but reactivity is specific for the α-F atoms. Monohalocarbene complexes are implicated as intermediates in the exchange process, as in the production of Re(CO)<sub>5</sub>CCl<sub>2</sub>CF<sub>3</sub> from the perfluoroethyl analogue

and BCl<sub>3</sub> (eq 16).<sup>71,72</sup> The same strategies used to stabilize dihalocarbene complexes relative to trihalomethyl complexes can be used to isolate a monohalocarbene derivative from a fluoroalkyl precursor (eq 32).<sup>73</sup>

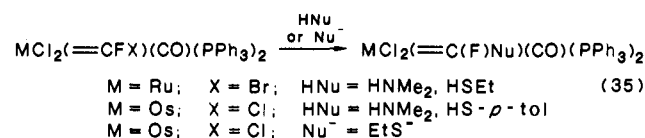


### 2. Nucleophilic Attack on Dihalocarbene Ligands

These reactions will be discussed in detail in section V and are mentioned here to survey the monohalocarbene complexes prepared by this method. The general reaction is that of a d<sup>6</sup> Ru, Os, or Ir dihalocarbene complex with an N-, O-, or S-atom nucleophile, as shown in eq 33 and 34.<sup>23-25,55,57,74,77</sup> In one example, pyrrole is the attacking nucleophile and substitutes at the carbene carbon to give a chloro-2-pyrrolylcarbene (eq 33).<sup>82a</sup>



When the mixed dihalocarbene species L<sub>n</sub>Ru=CBr and L<sub>n</sub>Os=CFCl are the substrates, in each case the F substituent remains and the Br or Cl is substituted.<sup>55,74,77</sup> This reflects both the stronger C-F bond and the better leaving group ability of Br or Cl relative to F (eq 35). The cationic osmium complex [OsCl(=CFCl)(MeCN)(CO)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup> reacts with HNMe<sub>2</sub> to give the corresponding cationic Os=C(F)NMe<sub>2</sub> complex.<sup>77</sup>



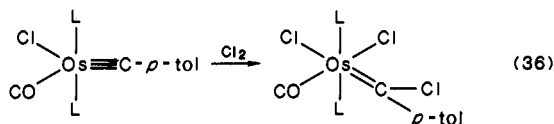
A number of the monohalocarbene complexes can themselves be derivatized by substitution reactions or by cation formation. These reactions illustrate the trans-labilizing influence of the carbene ligand. Several complexes prepared by substitution of the metal-bonded chloride ligand trans to the carbene ligand in the parent complex are [RuCl(=C(Cl)NMe<sub>2</sub>)(CO)-(PMe<sub>2</sub>Ph)<sub>3</sub>]ClO<sub>4</sub>, [RuCl(=C(Cl)NMe<sub>2</sub>)(CN-*p*-tol)(CO)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>, RuCl(SCN)(=C(Cl)NMe<sub>2</sub>)(CO)-(PPh<sub>3</sub>)<sub>2</sub>, [RuCl(=C(Cl)C<sub>4</sub>H<sub>4</sub>N)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>]SbF<sub>6</sub>, and [IrCl<sub>2</sub>(=C(Cl)NMe<sub>2</sub>)(MeCN)(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub>.<sup>24,57,82a</sup> The latter two complexes require Ag<sup>+</sup> ion to assist Cl<sup>-</sup> abstraction, but in the former examples the chloride is sufficiently labile that treatment with a suitable neutral or anionic ligand effects substitution. The fluoroaminocarbene complexes [RuCl(C(F)NMe<sub>2</sub>)(L)(CO)-(PPh<sub>3</sub>)<sub>2</sub>]ClO<sub>4</sub> (L = CN-*p*-tol, MeCN) were prepared similarly, the latter requiring the use of Ag<sup>+</sup>.<sup>23,55</sup> Finally, photolytic activation of substitution of PPh<sub>3</sub> for CO of Cr(=C(Cl)NMe<sub>2</sub>)(CO)<sub>5</sub> occurs at the cis position.<sup>82b</sup>

The wide variety of heteroatom-substituted monohalocarbene complexes prepared by these and other

methods reflects the stability conferred by the balance between the electron-withdrawing characteristic of the halide substituent and the electron-releasing  $\pi$ -donor property of the N, O, or S substituent.

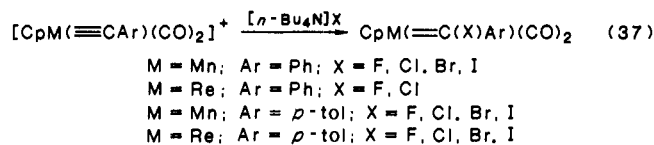
### 3. Metal Carbyne Complexes as Precursors

**a. Oxidative Addition.** The  $d^8$  osmium carbyne complex  $\text{OsCl}(\equiv\text{C-}p\text{-tol})(\text{CO})(\text{PPh}_3)_2$  oxidatively adds  $\text{Cl}_2$  across the  $\text{Os}\equiv\text{C}$  bond to give the chloro- $p$ -tolylcarbene complex shown in eq 36.<sup>83</sup> The  $p$ -tolylcarbyne

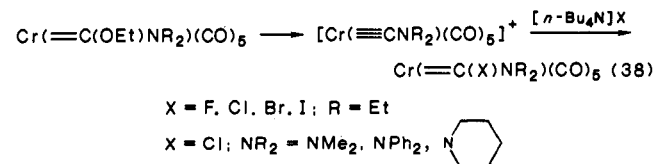


is itself produced from the dichlorocarbene complex  $\text{OsCl}_2(\equiv\text{CCl}_2)(\text{CO})(\text{PPh}_3)_2$  by reaction with  $\text{Li-}p\text{-tol}$  (vide infra) in a reaction not believed to involve the chloroarylcarbene complex as an intermediate.<sup>83</sup> Related complexes  $\text{MClX}(\equiv\text{CXPh})(\text{CO})(\text{PPh}_3)_2$  ( $\text{M, X} = \text{Os, Cl; Os, Br; Ru, Cl}$ ) are produced similarly.<sup>57</sup>

**b. Nucleophilic Attack.** In contrast to the neutral,  $d^8$  osmium carbyne complex which displays nucleophilic behavior, the cationic  $d^6$  manganese phenylcarbyne complex  $[\text{CpMn}(\equiv\text{CPh})(\text{CO})_2]\text{SbF}_6$  captures  $\text{F}^-$  to form a fluorophenylcarbene complex, characterized by an X-ray crystal structure determination.<sup>84</sup> This reaction is general for the Mn and Re cyclopentadienyl carbyne complexes shown in eq 37 and has been used to make complete series of halocarbyne complexes containing all four halide substituents.<sup>85</sup> Treatment of the manganese fluorophenylcarbene complex with  $\text{BF}_3$  reverses the reaction by  $\text{F}^-$  abstraction to form the  $\text{BF}_4^-$  salt of the carbyne precursor.<sup>84</sup>



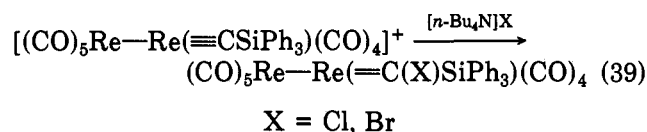
Several classical "Fischer-type" carbene complexes are precursors to monohalocarbene species. The first step of the reaction is treatment of  $\text{L}_n\text{M}=\text{C}(\text{OEt})\text{NEt}_2$  with  $\text{BF}_3$  to form a cationic carbyne complex,  $[\text{L}_n\text{M}(\equiv\text{CNEt}_2)]^+\text{BF}_4^-$ . As in the above manganese example, this species is treated with  $n\text{-Bu}_4\text{F}$  to form  $\text{L}_n\text{M}=\text{C}(\text{F})\text{NEt}_2$ . The fluoroaminocarbene species  $(\text{C}_5\text{H}_4(\text{CH}_3))\text{Mn}(\equiv\text{C}(\text{F})\text{NEt}_2)(\text{CO})_2$ <sup>84</sup> and the series  $\text{Cr}(\equiv\text{C(X)NR}_2)(\text{CO})_5$  ( $\text{X} = \text{F, Cl, Br, I}$ )<sup>86-88</sup> were prepared by this route from the analogous ethoxyaminocarbene species, shown in eq 38 for the chromium example.



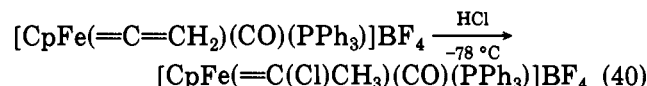
The reaction of the same chromium substrate with  $\text{BCl}_3$  or  $\text{BBr}_3$  results in direct formation of  $\text{Cr}(\equiv\text{C(X)NEt}_2)(\text{CO})_5$  ( $\text{X} = \text{Cl, Br}$ ) presumably via the same cationic carbyne intermediate.<sup>89</sup> The bromo- and chloroaminocarbene complexes are less stable than the fluoro congener, decomposing at  $-10$  and  $30$  °C, respectively, to  $\text{trans-CrX}(\equiv\text{CNEt}_2)(\text{CO})_4$ . The bromo-

and iodoaminocarbene complexes were characterized by spectroscopic means only.<sup>87</sup>

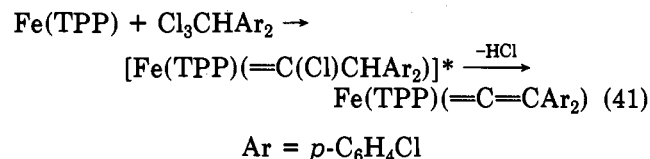
In a final example of halide capture by a carbyne complex, the novel bimolecular rhenium carbyne complex shown in eq 39 captures  $\text{Cl}^-$  or  $\text{Br}^-$  to form a (triphenylsilyl)halocarbene complex. The bromocarbene complex was characterized by spectroscopic means only.<sup>90</sup>



There is one report where a vinylidene complex serves as a precursor to a halocarbene complex by addition of  $\text{HCl}$  across the  $\text{C}=\text{C}$  bond as shown in eq 40. The

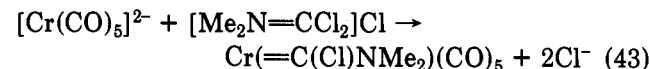
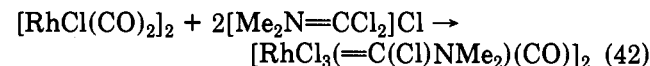


chloromethylcarbene product was characterized by NMR.<sup>91</sup> This process is actually the reverse of the reaction in which an iron porphyrin vinylidene complex is formed by treatment of the pesticide DDT (2,2-bis-( $p$ -chlorophenyl)-1,1,1-trichloroethane) with  $\text{Fe}(\text{TPP})$  under reducing conditions (eq 41).<sup>92</sup> The chlorocarbene intermediate is not observed but is presumed to be the precursor to the vinylidene species by loss of  $\text{HCl}$ , as in the reverse of eq 40.



### 4. Chloroaminocarbene Complexes Derived from an Iminium Salt

Chloro(dimethylamino)carbene complexes can, in several instances, be formed by transfer of the  $\text{C}(\text{Cl})\text{-NMe}_2$  fragment from the iminium salt  $[\text{Me}_2\text{N}=\text{CCl}_2]^+\text{Cl}^-$ .<sup>93</sup> Three fragment oxidative addition to a rhodium complex yields the chloroaminocarbene as in eq 42. A second complex,  $\text{RhCl}(\equiv\text{C}(\text{Cl})\text{NMe}_2)(\text{PPh}_3)_2$ , is formed similarly from  $\text{RhCl}(\text{PPh}_3)_3$ . A second mechanism is nucleophilic attack on the salt by a metal anion, producing  $\text{Mn}(\equiv\text{C}(\text{Cl})\text{NMe}_2)(\text{CO})_5$  from  $[\text{Mn}(\text{CO})_5]^-$  and the chromium example shown in eq 43.<sup>93</sup>



### 5. Metalloporphyrin Monohalocarbene Complexes

The reaction of  $\text{Fe}(\text{TPP})$  or  $\text{Fe}(\text{TPP})\text{Cl}$  with a geminal trihalide,  $\text{RCX}_3$ , in the presence of a reducing agent is a general route to a variety of iron monohalocarbene complexes. All complexes are iron(II), low-spin species that share with the parent dichlorocarbene complex a tendency to bind a sixth ligand.

Equation 44 demonstrates the utility of this route in preparing carbene complexes bearing both electron-withdrawing and electron-donating substituents.<sup>94,95</sup>



TABLE II. Structural Parameters for Monohalocarbene and Dihalocarbene Complexes

	M=C, Å	C-X, Å	XCX, deg	M-CO, Å	$\nu(\text{CX})$ , $\text{cm}^{-1}$	ref
Mono- and Dichlorocarbene Complexes						
[CpFe(=CCl <sub>2</sub> )(CO) <sub>2</sub> ]BCl <sub>4</sub> (7)	1.808 (12)	1.694 (12) 1.731 (11)	108.5 (7)	1.796 (12) 1.805 (10)	872, 860, 834, 810	32
Fe(TPP)(=CCl <sub>2</sub> )(OH) <sub>2</sub> <sup>a</sup> (13)	1.83 (3)	1.76 (3)	<i>b</i>		872	79
OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> <sup>a</sup> (21)						13
IrCl <sub>3</sub> (=CCl <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (25)	1.872 (7)	1.721 (5)	107.5 (4)		880, 810	25
Cr(=C(Cl)NEt <sub>2</sub> )(CO) <sub>5</sub> (35)	2.110 (5)	1.780 (6)	110.8 (4)	1.896 (cis) <sup>c</sup> 1.858 (trans)	<i>b</i>	98
RuCl <sub>2</sub> (=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (88)	1.949 (12)	1.826 (13)	104.4	1.857 (16)	784	82a
H <sub>2</sub> C=CCl <sub>2</sub>		1.710 (10)	114.5 (10)			99
H <sub>2</sub> C=CHCl		1.728 (7)				100
O=CCl <sub>2</sub>		1.742 (3)	124.0 (1)			101
:CCl <sub>2</sub>			106		746, 720	110
Mono- and Difluorocarbene Complexes						
[CpFe(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> )]BF <sub>4</sub> (5)	1.724 (9)	1.334 (10)	98.3 (7)	1.798 (10)	1233, 1200	32
Ru(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (26)	1.83 (1)	1.37 (1) 1.36 (1)	88.7 (9)	1.87 (1) 1.91 (2)	1083, 980	76
Os(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (27)	1.915 (15)	1.331 (18) 1.407 (17)	101.4 (12)	1.884 (13) 1.938 (15)	1122, 990	7
OsCl(NO)(=CF <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (30)	1.967 (6)	1.278 (11) 1.285 (11)	105.0 (7)		1154, 1020	6
Ir(CF <sub>3</sub> )(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (32)	1.874 (7)	1.30 (2) 1.30 (1)	89.5 (8)	1.874 (7)	1165, 1060, 1005	37
CpMn(=C(F)Ph)(CO) <sub>2</sub> (48)	1.830 (5)	1.392 (6)	106.1 (4)	1.784 (6) 1.795 (6)	<i>b</i>	84
RuCl <sub>2</sub> (=C(F)OCH <sub>2</sub> CM <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (77)	1.914 (5)	1.307 (6)	107.4 (5)	1.910 (7)	<i>b</i>	77
CF <sub>2</sub> =CF <sub>2</sub>		1.31 (1)	114 (2)			106
CH <sub>2</sub> =CF <sub>2</sub>		1.321	110			106
O=CF <sub>2</sub>		1.316 (1)	107.7 (1)			107
:CF <sub>2</sub>		1.30	105		1222, 1102	22, 111

<sup>a</sup> Disordered structure. <sup>b</sup> Data not reported. <sup>c</sup> Average value.

The cyano- and ethoxycarbonyl complexes are much more susceptible to nucleophilic attack than the more electron-rich chloroalkylcarbene species.<sup>94</sup>



X = Cl; R = CN, CO<sub>2</sub>Et, CH<sub>3</sub>, CH<sub>2</sub>OH, CHMeOH, CHPhOH, CMe<sub>2</sub>OH  
X = Br; R = CH<sub>2</sub>OH

The trichloromethyl thio- and selenoethers PhCH<sub>2</sub>YCCl<sub>3</sub> (Y = S, Se) proved to be precursors to the chlorocarbene complexes Fe(TPP)(C(Cl)YCH<sub>2</sub>Ph). Related substrates RSCCl<sub>3</sub> (R = Ph, phthalimido) reacted similarly to give the corresponding iron complexes containing the C(Cl)SR ligand.<sup>45,96</sup> An attempt to prepare chlorocarbene complexes with  $\alpha$ -silyl groups by using Cl<sub>3</sub>CSiMe<sub>3</sub> as the carbene source proved unsuccessful, leading to retention of the metal-carbon bond but loss of the chloro and trimethylsilyl substituents.<sup>97</sup>

#### IV. Structural and Spectroscopic Properties

##### A. Structural Results

X-ray crystal structure determinations have been carried out for five difluorocarbene, four dichlorocarbene, and four monohalocarbene complexes. The small number of structures, among which the metal, oxidation state, and ancillary ligands vary, and the lack of isostructural examples containing other carbene ligands make it difficult to draw direct comparisons, although a few general trends are apparent. The M=C, C-X, and M-CO bond lengths, the XCX bond angle, and  $\nu(\text{CX})$  values are shown in Table II for all of these compounds except OsCl<sub>2</sub>(=CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (21), in which a disorder problem seriously diminishes the re-

liability of the metrical data.<sup>13</sup> The structure of the iron porphyrin complex 13 is also disordered.<sup>79</sup> Large thermal parameters resulting in high standard deviations were observed for the fluorine atoms in some structures. Representative structures of a dichlorocarbene and a difluorocarbene complex are shown in Figures 2 and 3.

For each structure, the sum of angles around the carbene carbon atom is very close to 360°, consistent with an sp<sup>2</sup>-hybridized carbon atom. All structures, except perhaps the chromium chloroaminocarbene complex Cr(=C(Cl)NEt<sub>2</sub>)(CO)<sub>5</sub> (35),<sup>98</sup> exhibit short M=C bond lengths as expected for some degree of metal-carbon multiple bonding. The structural data also support the spectroscopic evidence (vide infra) which indicates the good  $\pi$ -acceptor capabilities of the CX<sub>2</sub> ligands. Each compound containing both CX<sub>2</sub> and CO ligands has a metal-carbene distance which is comparable to (complexes 7, 27, 32) or shorter than (complexes 5, 26) the metal-carbonyl distance.

The octahedral Ru complexes RuCl<sub>2</sub>(=C(Cl)C<sub>4</sub>H<sub>4</sub>N)(CO)(PPh<sub>3</sub>)<sub>2</sub> (88)<sup>82</sup> and RuCl<sub>2</sub>(=C(F)OCH<sub>2</sub>CM<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (77)<sup>77</sup> and the Os complex OsCl<sub>2</sub>(=CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (21)<sup>13</sup> confirm the geometry expected for all the group 8 examples of the general formula MX<sub>2</sub>(carbene)(L)(PPh<sub>3</sub>)<sub>2</sub>, with trans PPh<sub>3</sub> and cis halide ligands. In addition, complexes 88 and 77 and the iridium complex IrCl<sub>3</sub>(=CCl<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> (25)<sup>25</sup> show that the carbene ligand has a pronounced structural trans influence. In these structures the M-Cl bond trans to the carbene ligand is approximately 0.05 Å longer than that cis to the carbene. The geometry of the iridium complex 25 is shown in Figure 2.<sup>25</sup> The iridium, carbene carbon, and trans chloride atoms lie on a crystallographically imposed twofold axis. The planar CCl<sub>2</sub> ligand is tilted at an angle of 24.4° relative

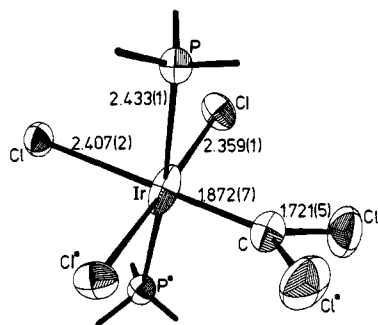
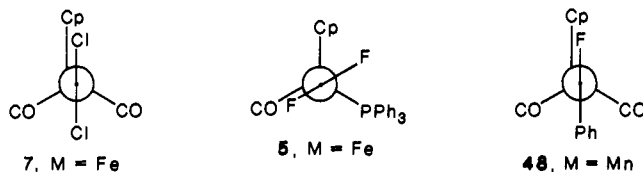


Figure 2. Crystal structure of  $\text{IrCl}_3(=\text{CCl}_2)(\text{PPh}_3)_2$ .

to the plane containing the three chloride ligands. This angle is quite variable; in the other octahedral complexes 88, 21, and 77 the carbene ligand is coplanar with the equatorial plane of the complex, while in the porphyrin complex 13 and the pentacarbonylchromium complex 35 the carbene ligand is tilted. The C-Cl distances in the dihalocarbene complexes  $[\text{CpFe}(=\text{CCl}_2)(\text{CO})_2]\text{BCl}_3$  (7)<sup>32</sup> and  $\text{Fe}(\text{TPP})(=\text{CCl}_2)$  (13)<sup>79</sup> and the iridium complex 25<sup>25</sup> are very close to those observed for the  $\text{C}(\text{sp}^2)\text{-Cl}$  bonds in 1,1-dichloroethylene,<sup>99</sup> vinyl chloride,<sup>100</sup> and phosgene<sup>101</sup> (Table II). In contrast, the two monohalocarbene complexes 35 and 88 show significantly lengthened C-Cl bonds.

It is interesting to compare the geometry of three cyclopentadienyl derivatives,  $[\text{CpFe}(=\text{CF}_2)(\text{CO})(\text{PPh}_3)]\text{BF}_4$  (5),<sup>32</sup>  $\text{CpMn}(=\text{CFPh})(\text{CO})_2$  (48),<sup>84</sup> and the iron  $\text{CCl}_2$  complex 7. The Newman-type projections



illustrate that in the dicarbonyl complexes 7 and 48 the plane of the carbene ligand bisects the  $(\text{CO})\text{M}(\text{CO})$  angle, whereas in the less symmetrical complex 5 the carbene plane is aligned with the CO ligand.<sup>32,84</sup> These conformations are predicted by extended Hückel and Fenske-Hall theory. Calculations for complexes of the general formula  $\text{CpM}(\text{carbene})\text{LL}'$  suggest that in symmetrical complexes ( $\text{L} = \text{L}'$ ) the carbene will lie in the plane bisecting the  $\text{LML}'$  angle, while in unsymmetrical structures the carbene is expected to be coplanar with the better  $\pi$  acceptor,<sup>102-104</sup> as observed in complex 5. The geometries of other structurally characterized complexes in this class are also consistent with the theoretical predictions.<sup>32,84</sup> In the manganese fluoro-phenylcarbene complex 48 the bulky phenyl substituent is oriented away from the cyclopentadienyl ring.

The first-row metal Mn and Fe complexes 5, 7, 13, and 48 in general exhibit shorter  $\text{M}=\text{C}$  bonds than do the other examples in Table II which contain second- and third-row metals. Comparing the cyclopentadienyl derivatives 5, 7, 48, and  $\text{CpMn}(=\text{CPh}_2)(\text{CO})_2$ <sup>105</sup> the  $\text{M}=\text{C}$  bond is shortest (1.72 Å) in the  $\text{Fe}=\text{CF}_2$  complex 5, demonstrating that  $\text{CF}_2$  is the best  $\pi$  acceptor of the four carbene ligands. The  $\text{Fe}=\text{CCl}_2$  and  $\text{Mn}=\text{CFPh}$  bonds are comparable (1.808 and 1.830 Å), and the  $\text{Mn}=\text{CPh}_2$  is the longest at 1.885 Å. The  $\text{XCX}$  bond angle follows a similar order; smallest for the  $\text{Fe}=\text{CF}_2$  complex 5 (98.5°), comparable for 7 and 48, and largest

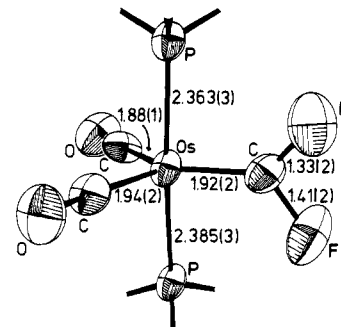


Figure 3. Crystal structure of  $\text{Os}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$ .

for the  $\text{Mn}=\text{CPh}_2$  complex (112.7°).<sup>105</sup>

The three zerovalent Ru and Os difluorocarbene complexes  $\text{Ru}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$  (26),<sup>76</sup>  $\text{Os}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$  (27),<sup>6</sup> and  $\text{OsCl}(\text{NO})(=\text{CF}_2)(\text{PPh}_3)_2$  (30)<sup>7</sup> are the most closely related to the structures presented in Table II. Data for tetrafluoroethylene,<sup>106</sup> difluoroethylene,<sup>106</sup> carbonyl fluoride,<sup>107</sup> and free  $:\text{CF}_2$ <sup>21,22</sup> are included in Table II for comparison. All three complexes are trigonal-bipyramidal and contain trans  $\text{PPh}_3$  ligands in the axial sites, as illustrated by the structure of  $\text{Os}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$  (30)<sup>6</sup> in Figure 3. The difference in the two C-F bond lengths in this structure is probably a result of the large thermal parameters associated with the fluorine atoms. Figure 3 also shows the vertical orientation (with respect to the equatorial plane) adopted by the carbene ligand in all the  $\text{d}^8$  structures. This is in contrast to the in-plane conformation observed for olefin complexes of  $\text{d}^8$  metal centers.<sup>108</sup> However, for a coordinated olefin in this conformation, the orbitals of  $\pi$  symmetry are oriented in the equatorial plane. The  $\pi$  orbital of the carbene ligand has the same orientation,<sup>14</sup> and since olefin and carbene ligands are related by the isolobal analogy, the vertical conformation is expected for  $\text{d}^8$  carbene complexes.<sup>109</sup>

The  $\text{d}^8$  iridium(I) complex  $\text{Ir}(\text{CF}_3)(=\text{CF}_2)(\text{CO})(\text{PPh}_3)_2$  (32),<sup>37</sup> while exhibiting the same trigonal-bipyramidal geometry as the  $\text{d}^8$  Ru and Os examples, is unusual in containing cis triphenylphosphine ligands. The axial sites are occupied by one phosphine and the trifluoromethyl group, and the  $\text{CF}_2$  ligand takes up a vertical orientation in the axial plane. The unusual cis geometry may be the result of competition for electron density between the strongly electron-withdrawing CO,  $\text{CF}_2$ , and  $\text{CF}_3$  ligands. However <sup>31</sup>P NMR data indicates that both isomers are present in solution, although interconverting only slowly.<sup>37</sup>

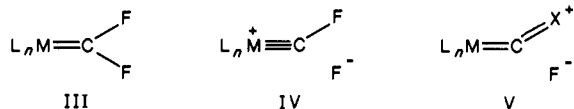
Comparison of the structural and IR data for the group 8 complexes 26, 27, and 30 does indicate a trend. The short  $\text{M}=\text{C}$  bond, long C-F bond, low  $\nu(\text{CF})$  value, and small FCF angle of  $\text{Ru}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$  vary through  $\text{Os}(=\text{CF}_2)(\text{CO})_2(\text{PPh}_3)_2$  to the long  $\text{M}=\text{C}$  and short C-F bonds, high  $\nu(\text{CF})$  value, and large FCF angle of  $\text{OsCl}(\text{NO})(=\text{CF}_2)(\text{PPh}_3)_2$ . Thus strong  $\text{M}=\text{C}$  bonding is associated with weak C-F bonding in the electron-rich Ru complex 26, and the opposite is true for the osmium complex 30. Chemical evidence suggests that the " $\text{OsCl}(\text{NO})(\text{PPh}_3)_2$ " fragment is less electron rich than " $\text{Os}(\text{CO})_2(\text{PPh}_3)_2$ ",<sup>57</sup> resulting in more effective  $\text{M}=\text{CF}_2$   $\pi$  bonding for the latter.

Several explanations may be made to account for the relationships between bond lengths and angles in

fluorocarbene complexes. One possibility, which is supported by the trends described for the zerovalent group 8  $\text{CF}_2$  complexes, is that fluorine may function as a  $\pi$  donor toward the carbene carbon atom.<sup>6</sup> Effective fluorine to carbon  $\pi$  donation would be apparent when a short C-F bond is associated with a longer M=C bond as observed for  $\text{OsCl}(\text{NO})(=\text{CF}_2)(\text{PPh}_3)_2$ . A more electron-rich metal center should result in a negligible C-F  $\pi$  interaction with a corresponding reversal in the relative bond lengths. Although this proposal is attractive, the number of compounds available for comparison is too limited to establish definitively the possibility of fluorine  $\pi$  donation.

Short M=C bonds in mono- and difluorocarbene complexes have also been attributed to Bent's rule, which suggests that hybrid orbitals involved in bonding to an electronegative atom will be depleted in s character, causing a shortening of the other bonds to the central atom, and that the XCX angle should decrease as the electronegativity of X becomes greater.<sup>32</sup> Increases in both M=C bond length and XCX angle in the series  $[\text{CpFe}(\text{CF}_2)(\text{CO})(\text{PPh}_3)]^+$ ,  $\text{CpMn}(\text{CFPh})(\text{CO})_2$  and  $\text{CpMn}(\text{CPh}_2)(\text{CO})_2$  were rationalized by this hypothesis.<sup>32</sup> Thus a relative increase in the amount of p character in the orbitals bonding to electronegative carbene substituents would lead to longer C-F bonds and a smaller FCF angle, without invoking C-F  $\pi$  bonding.

One further suggestion put forward to rationalize the structural parameters observed for fluorocarbene complexes is hyperconjugation of the metal and fluorine centers, involving resonance structures III and IV.<sup>84</sup> This is similar to the hyperconjugation argument proposed to explain the short M-C and long C-F bonds in transition-metal  $\text{CF}_3$  complexes, discussed in section III.A. Hyperconjugation of the two carbene substituents in a monofluorocarbene complex would involve structure V. If contributions from any of these reso-

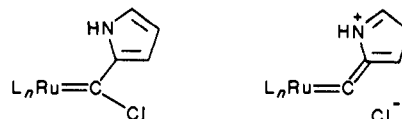


nance forms were significant, then fluorocarbenes might be expected to be precursors to carbyne or isocyanide complexes prepared by F atom abstraction. However, although reactions of this type have been observed for chloroaminocarbene complexes, the corresponding fluoroaminocarbene species were unreactive.<sup>88,87,89</sup> In one example where such a reaction has been reported, the carbyne complex  $[\text{CpMn}(\text{CPh})(\text{CO})_2]^+$  is produced by  $\text{BF}_3$ -mediated fluoride abstraction from  $\text{CpMn}(\text{CFPh})(\text{CO})_2$ .<sup>84</sup>

It is difficult to find any trends in the structural parameters of the two monochlorocarbene (35, 88) and two monofluorocarbene complexes (48, 77) reported in Table II. All show M=C bonds longer than their dihalocarbene analogues, as expected for the less effective  $\pi$ -acceptor monohalocarbene ligands. The metal-carbene bond in the chromium complex 35 is longer than any CO ligand in the complex, reflecting competition with the five CO ligands for metal electron density and efficient  $\pi$  donation by the diethylamino substituent. This latter effect also results in a shorter M-CO bond in the position trans to the carbene than in the cis positions.

The ruthenium complex 48 offers an internal comparison between the two C-O bonds of the  $\text{Ru}=\text{C}(\text{F})\text{OCH}_2\text{CMe}_3$  fragment. The carbene carbon-oxygen distance of 1.303 (7) Å is much shorter than the oxygen-neopentyl carbon distance of 1.479 (8) Å, even taking into account the difference in radii of  $\text{sp}^2$  and  $\text{sp}^3$  carbons.<sup>77</sup> This suggests a degree of multiple-bonding character in the carbene-oxygen bond, as a result of  $\pi$  donation from oxygen to carbon.

The angles around the carbene carbon in  $\text{RuCl}_2(\text{C}(\text{F})\text{OCH}_2\text{CMe}_3)(\text{CO})(\text{PPh}_3)_2$  (77) are normal, but the M=CXR complexes 35, 48, and 88 all show marked decreases in the CrCX angle (113.8°, 116.4°, and 117.5°) and increases in the CrCR angle (135.4°, 139.2°, and 136.4°, respectively). These data suggest a contribution from the resonance structures proposed above for the hyperconjugation argument, where for the Cr and Ru complexes 35 and 88, structure V may be more important than III or IV on account of the relatively long M=C bond lengths. The data for the chloro-2-pyrrolylcarbene complex 88 are particularly convincing, with a short C(carbene)-C(pyrrole) bond and alternation of the bonds around the pyrrole ring consistent with the resonance structure shown below.



Other notable features of this structure are the coplanarity of the carbene and pyrrole fragments and the strong intramolecular hydrogen bond between the pyrrole NH and the metal-bonded chloro ligand in the position cis to the carbene.<sup>82</sup>

Finally, the bonding scheme outlined in section II implicated geometrical differences between covalent and donor/acceptor bonding in metal carbene complexes. The geometries calculated for both covalent and donor/acceptor states of the model ruthenium methylenide species  $\text{RuCH}_2^+$  resulted in a prediction that lengthening of the metal carbon bond and a decrease in the HCH angle should occur on going from covalent to donor/acceptor bonding.<sup>17</sup> The isostructural complexes  $\text{OsCl}(\text{NO})(=\text{CH}_2)(\text{PPh}_3)_2$ <sup>11</sup> and  $\text{OsCl}(\text{NO})(=\text{CF}_2)(\text{PPh}_3)_2$ <sup>7</sup> were suggested as examples of each type of bonding, respectively.<sup>17</sup> The lengthening of the Os=C bond from 1.92 (1) Å in the methylene complex to 1.976 (6) Å in the difluorocarbene complex is consistent with this prediction. Unfortunately these complexes represent the only matched pair of alkylidene and dihalocarbene species to be structurally characterized. This problem pinpoints the need for much more structural investigation of halocarbene complexes, with attention being paid to the choice of examples from which useful comparisons may be made. Again, this returns to the need for the synthetic flexibility and diversity required to achieve this goal.

## B. IR Spectroscopy

In general, C-F and C-Cl stretching frequencies can be identified in the IR spectra of halocarbene complexes. These data are collected in Table III, together with  $\nu(\text{CO})$  values. For dihalocarbene species two C-X bands are observed, ranging from 880 to 770  $\text{cm}^{-1}$  for the  $\text{CCl}_2$  group. Free  $:\text{CCl}_2$  has  $\nu(\text{C-Cl})$  values of 746 and

720  $\text{cm}^{-1}$ .<sup>110</sup> A  $\nu(\text{CBr})$  value has been reported for only one compound, 805  $\text{cm}^{-1}$  for  $\text{RuBr}_2(\text{=CFBr})(\text{CO})(\text{PPh}_3)_2$ .<sup>6,74</sup>

The greater diversity found for  $\text{CF}_2$  complexes, including compounds in different oxidation states for the same metal, results in a wide range of values for the two  $\nu(\text{CF})$  bands, from 1233 to 980  $\text{cm}^{-1}$ . Table II demonstrates that among similar compounds a high  $\nu(\text{CF})$  value corresponds to a short C-F bond length and vice versa. High  $\nu(\text{CF})$  values are also associated with electrophilic behavior at the carbene carbon atom (1210 and 1184  $\text{cm}^{-1}$  for  $\text{RuCl}_2(\text{=CF}_2)(\text{CO})(\text{PPh}_3)_2$ )<sup>23</sup> and low  $\nu(\text{CF})$  values with nucleophilic reactivity (1083 and 980  $\text{cm}^{-1}$  for  $\text{Ru}(\text{=CF}_2)(\text{CO})_2(\text{PPh}_3)_2$ )<sup>76</sup>. These values compare with 1222 and 1102  $\text{cm}^{-1}$  observed for free  $:\text{CF}_2$ .<sup>111</sup> Correlation of bond strength with stretching frequency suggests that the C-F bonds in the Ru(II) complex are as strong as those in the free carbene.

The  $\nu(\text{CF})$  value for difluorocarbenes is useful in the same way as  $\nu(\text{CO})$  for metal carbonyls, as an indicator of the electronic interaction at the metal center. For example, electrophilic behavior at the CO carbon atom is indicated by a high  $\nu(\text{CO})$  value. Changes in the coordination sphere of a metal carbonyl complex affect  $\nu(\text{CO})$ , and  $\nu(\text{CX})$  values of halocarbene species are sensitive in the same way. Examples in Table III illustrate that going from a neutral to a cationic species causes an increase in  $\nu(\text{CX})$ . When the axial ligand in  $\text{Fe}(\text{TPP})(\text{CCl}_2)\text{L}$  is changed from  $\text{H}_2\text{O}$  to pyridine,  $\nu(\text{CCl})$  drops from 872 to 863  $\text{cm}^{-1}$ , reflecting the effect on the carbene ligand of the more electron-rich pyridine in the trans position.<sup>79</sup>

Values of  $\nu(\text{CX})$  are more difficult to observe for monohalocarbene complexes. Within the series of groups 8 and 9 monohalocarbene triphenylphosphine complexes,  $\text{L}_n\text{M}=\text{CXR}$ , there is little effect on  $\nu(\text{CX})$  as R varies among  $\text{NR}_2$ , OR, or SR groups, although as expected,  $\nu(\text{CCl})$  is much higher for R = F (885  $\text{cm}^{-1}$ ) than for R =  $\text{NMe}_2$  (790  $\text{cm}^{-1}$ ) or *p*-tol (800  $\text{cm}^{-1}$ ) in  $\text{OsCl}_2(\text{=CClR})(\text{CO})(\text{PPh}_3)_2$ .<sup>57,77,83</sup>

The  $\nu(\text{CO})$  value is a good probe into the relative  $\sigma$ -donor and  $\pi$ -acceptor properties of other ligands in the coordination sphere. The value of  $\nu(\text{CO})$  for complexes  $\text{ML}(\text{CO})_2(\text{PPh}_3)_2$  containing different neutral ligands L decreases in the order  $\text{L} = \text{CF}_2 \approx \text{CTe} > \text{CSe} > \text{CS} > \text{CN-}p\text{-tol}$ , which supports the conclusion drawn from the structural data that the  $\text{CF}_2$  ligand must be an exceptionally good  $\pi$  acceptor.<sup>55</sup> The  $\nu(\text{CO})$  value for the complex  $\text{RuCl}_2(\text{=CF}_2)(\text{CO})(\text{PPh}_3)_2$  (2035, 2014  $\text{cm}^{-1}$ ) is much higher than for complexes with  $\pi$ -donor substituents on the carbene ligand,  $\text{RuCl}_2(\text{=C}(\text{F})\text{SEt})(\text{CO})(\text{PPh}_3)_2$  (1995  $\text{cm}^{-1}$ )<sup>74</sup> and  $\text{RuCl}_2(\text{=C}(\text{SMe})_2)(\text{CO})(\text{PPh}_3)_2$  (1950  $\text{cm}^{-1}$ ).<sup>24</sup> Similarly,  $\nu(\text{CO})$  for  $\text{OsCl}_2(\text{=CXPh})(\text{CO})(\text{PPh}_3)_2$  drops from 1960 to 1945  $\text{cm}^{-1}$  when X = Cl is replaced by H.<sup>57</sup> A comparison of  $\nu(\text{NO})$  for  $\text{OsCl}(\text{NO})(\text{=CF}_2)(\text{PPh}_3)_2$  (1650  $\text{cm}^{-1}$ )<sup>7</sup> and  $\text{OsCl}(\text{NO})(\text{=CH}_2)(\text{PPh}_3)_2$  (1628  $\text{cm}^{-1}$ )<sup>11</sup> shows that  $\text{CF}_2$  is a better  $\pi$  acceptor than  $\text{CH}_2$ .

Table III shows that for the series  $\text{CpMn}(\text{=C}(\text{X})p\text{-tol})(\text{CO})_2$ ,  $\nu(\text{CO})$  increases along the series  $\text{F} < \text{Cl} < \text{Br} < \text{I}$ ,<sup>85</sup> which is opposite to the order expected for decreasing  $\pi$  acceptance by the carbene ligand along the series. This reflects the sensitivity of  $\nu(\text{CO})$  to the  $\sigma$ -donor/ $\pi$ -acceptor ratio rather than to  $\pi$  effects alone, and this ratio must be decreasing along the series.

Similarly, the  $\sigma$ -donor/ $\pi$ -acceptor ratio is higher for  $\text{Cr}(\text{=C}(\text{OEt})\text{NEt}_2)(\text{CO})_5$  than for  $\text{Cr}(\text{=C}(\text{Cl})\text{NEt}_2)(\text{CO})_5$ .<sup>88</sup>

### C. NMR Spectroscopy

Table IV collects  $^{13}\text{C}$  NMR data for the carbene carbon atoms and  $^{19}\text{F}$  NMR data for fluorine substituents in halocarbene complexes. Although proton data have been recorded for many of the complexes discussed here, it does not contribute greatly to our understanding of their chemistry. One notable detail of the  $^1\text{H}$  NMR spectra is that for many of the halaminocarbene complexes, restricted rotation about the C-N bond on the NMR time scale results in two sets of resonances for the two substituents on the nitrogen, reflecting Z or E geometry with respect to the halide substituent.<sup>23,88</sup> Unfortunately,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR data, which are much more useful to this discussion, are very limited in scope, as shown by the small number of entries in Table IV. Difficulty in observing the resonance of the carbene carbon is often encountered for  $\text{CF}_2$  complexes, especially when phosphine ligands are also present, because of splitting due to spin-spin coupling.<sup>32,37</sup> The following observations made from the NMR results are qualified by the limited amount of data reported in the literature.

The  $^{13}\text{C}$  NMR data in Table IV show that the resonances of the carbene carbon atoms are deshielded and fall into the 200–400 ppm range typical of all carbene and alkylidene ligands.<sup>4,7,8</sup> It is difficult to compare halocarbene complexes to analogues without halide substituents. For example, the CXY resonance in  $[\text{RuCl}(\text{=CXY})(\text{CO})(\text{CN-}p\text{-tol})(\text{PPh}_3)_2]^+$  is downfield for X, Y = Cl,  $\text{NMe}_2$  (222 ppm) relative to X, Y =  $\text{HNC-}p\text{-tol}$  (201 ppm),<sup>57</sup> and the carbene carbon in  $\text{Cr}(\text{=C}(\text{X})\text{NEt}_2)(\text{CO})_5$  resonates further downfield for X = Cl than for X = OEt.<sup>88</sup> In contrast, the opposite effect is observed for X = Cl or OMe in  $\text{Fe}(\text{TPP})(\text{=C}(\text{X})\text{CHMe}_2)$ .<sup>94,96</sup>

In the series of similar complexes  $\text{Cr}(\text{=C}(\text{X})\text{NEt}_2)(\text{CO})_5$ , the chemical shift of the carbene carbon atom is almost insensitive to change as X varies through F, Cl, Br. The iron porphyrin carbene series  $\text{Fe}(\text{TPP})(\text{=C}(\text{Cl})\text{R})$  shows a much greater effect. As R changes from electron-rich (alkyl) substituents to the strongly electron-withdrawing substituents like CN and  $\text{CO}_2\text{Et}$ , the chemical shift of the carbene carbon spans a range of over 100 ppm, from 324 to 210 ppm. The carbene ligands with the more electron-withdrawing substituents exhibit the upfield resonances, consistent with the general observation for transition-metal carbene complexes that this resonance moves to higher field as the complex becomes more electron-deficient.<sup>7</sup>

The  $^{19}\text{F}$  NMR data for fluorocarbene complexes are extremely limited and are complicated by differences in reference and sign conventions reported in the literature. The data for the molybdenum species illustrate that the carbene  $^{19}\text{F}$  resonance is significantly upfield for the monofluorocarbene complex relative to the  $\text{CF}_2$  complexes.<sup>73</sup> However, the opposite effect is true for the iron complexes in which the CFCl resonance is downfield of the  $\text{CF}_2$  resonance.<sup>32</sup> In  $[\text{CpMo}(\text{=C}(\text{F})\text{CF}_2\text{CF}_3)(\text{CO})_3]\text{SbF}_6$ , the fluorine bonded to the carbene carbon is significantly deshielded compared to the fluorines in the fluoroethyl group. This is exactly

TABLE III. IR Data for Dihalocarbene and Monohalocarbene Complexes<sup>a</sup>

	$\nu(\text{CF}), \text{cm}^{-1}$	$\nu(\text{CCl}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	ref
Dihalocarbene Complexes				
[CpMo(=CF <sub>2</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub> <sup>b</sup> (1)				73
[CpMo(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> )]SbF <sub>6</sub> <sup>b</sup> (2)				73
[Mn(=CF <sub>2</sub> )(CO) <sub>5</sub> ]BF <sub>4</sub> <sup>b</sup> (3)				31
[CpFe(=CF <sub>2</sub> )(CO) <sub>2</sub> ]BF <sub>4</sub> (4)	1233, 1200		2115, 2071	31
[CpFe(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> )]BF <sub>4</sub> (5)	1198, 1182		2024	32
[CpFe(=CFCl)(CO)(PPh <sub>3</sub> ) <sup>+</sup> ] <sup>b</sup> (6)				32
[CpFe(=CCl <sub>2</sub> )(CO) <sub>2</sub> ]BCl <sub>4</sub> (7)		872, 860, 834, 810	2107, 2078 <sup>c</sup>	31
[CpFe(=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sup>+</sup> ] <sup>b</sup> (8)				32
[CpFe(=CBr <sub>2</sub> )(CO) <sub>2</sub> ]BBr <sub>4</sub> <sup>b</sup> (9)			2105, 2078 <sup>c</sup>	31
Fe(TPP)(=CF <sub>2</sub> ) <sup>b</sup> (10)				45
Fe(TPP)(=CFCl) (11)				45
Fe(TPP)(=CFBr) (12)				45
Fe(TPP)(=CCl <sub>2</sub> )(OH <sub>2</sub> ) (13)		872 (841 <sup>d</sup> )		10, 79
Fe(TPP)(=CBr <sub>2</sub> ) (14)				45
RuCl <sub>2</sub> (=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (15)	1210, 1184, 1155, 1138		(2035, 2014) <sup>e</sup>	23
RuBr <sub>2</sub> (=CFBr)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (16)	1140, 1027		(2040, 2020) <sup>e</sup>	74
OsCl <sub>2</sub> (=CFCl)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (17)	1124	885	(2008, 1990) <sup>e</sup>	77
[OsCl(=CFCl)(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (18)	1125	909	2018	77
RuCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (19)		860, (790, 780) <sup>e</sup>	(2030, 2005) <sup>e</sup>	24
[RuCl(=CCl <sub>2</sub> )(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (20)		865, 812	2030	57
OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (21)		880, (780, 770) <sup>e</sup>	(2012, 1990) <sup>e</sup>	13
[OsCl(=CCl <sub>2</sub> )(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (22)		890, 790	2020	78
OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CS)(PPh <sub>3</sub> ) <sub>2</sub> (23)		864, 770		13
[OsCl(=CCl <sub>2</sub> )(MeCN)(CS)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (24)		882, 795		57
IrCl <sub>3</sub> (=CCl <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (25)		880, 810		35
Ru(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (26)	1083, 980		1983, 1910	76
Os(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (27)	1122, 990		1975, 1905	6, 7
Os(=CF <sub>2</sub> )(CO)(CS)(PPh <sub>3</sub> ) <sub>2</sub> (28)	1100, 990		(1950, 1934) <sup>e</sup>	6, 7
RuCl(NO)(=CF <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (29)	1142, 1022			6, 7
OsCl(NO)(=CF <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (30)	1154, 1020			6, 7
IrI(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (31)	1170, 1060		1970	37
Ir(CF <sub>3</sub> )(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (32)	1165, 1060, 1005		1975	37
Monohalocarbene Complexes				
[CpMo(=C(F)C <sub>2</sub> F <sub>5</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub> (33)	1210-1180		2035, 2120	73
Cr(=C(F)NEt <sub>2</sub> )(CO) <sub>5</sub> (34)			2064, 1930 <sup>c</sup>	86
Cr(=C(Cl)NEt <sub>2</sub> )(CO) <sub>5</sub> (35)			2059, 1930 <sup>c</sup>	88, 89
Cr(=C(Br)NEt <sub>2</sub> )(CO) <sub>5</sub> (36)			2057, 1923 <sup>c</sup>	87, 89
Cr(=C(I)NEt <sub>2</sub> )(CO) <sub>5</sub> (37)			2064, 1939 <sup>f</sup>	87
Cr(=C(Cl)NMe <sub>2</sub> )(CO) <sub>5</sub> (38)		779	2063, 1939 <sup>g</sup>	88, 93
Cr(=C(Cl)N(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> )(CO) <sub>5</sub> (39)			2062, 1939 <sup>g</sup>	88
Cr(=C(Cl)NPh <sub>2</sub> )(CO) <sub>5</sub> (40)			2065, 1954 <sup>h</sup>	88
cis-Cr(=C(Cl)NMe <sub>2</sub> )(CO) <sub>4</sub> (PPh <sub>3</sub> ) (41)				82b
[Mn(=C(Cl)NMe <sub>2</sub> )(CO) <sub>5</sub> ]ClO <sub>4</sub> (42)		826		93
( $\eta^5$ -C <sub>5</sub> H <sub>4</sub> CH <sub>3</sub> )Mn(=C(F)NEt <sub>2</sub> )(CO) <sub>2</sub> (43)			1927, 1853 <sup>c</sup>	84
CpMn(=C(F) <i>p</i> -tol)(CO) <sub>2</sub> (44)			1986, 1923 <sup>c</sup>	85
CpMn(=C(Cl) <i>p</i> -tol)(CO) <sub>2</sub> (45)			1988, 1936 <sup>c</sup>	85
CpMn(=C(Br) <i>p</i> -tol)(CO) <sub>2</sub> (46)			2000, 1946 <sup>c</sup>	85
CpMn(=C(I) <i>p</i> -tol)(CO) <sub>2</sub> (47)			2002, 1948 <sup>c</sup>	85
CpMn(=C(F)Ph)(CO) <sub>2</sub> (48)				84
CpMn(=C(X)Ph)(CO) <sub>2</sub> (X = Cl, Br, I) (49-51)				85
CpRe(=C(X)Ph)(CO) <sub>2</sub> (X = F, Cl) (52, 53)				85
CpRe(=C(X) <i>p</i> -tol)(CO) <sub>2</sub> (X = F, Cl, Br, I) (54-57)				85
(CO) <sub>5</sub> Re-Re(=C(Cl)SiPh <sub>3</sub> )(CO) <sub>4</sub> (58)				90
(CO) <sub>5</sub> Re-Re(=C(Br)SiPh <sub>3</sub> )(CO) <sub>4</sub> (59)				90
[CpFe(=C(Cl)Me(CO)(PPh <sub>3</sub> )](PPh <sub>3</sub> )BF <sub>4</sub> <sup>b</sup> (60)			1990 <sup>c</sup>	91
Fe(TPP)(=C(Cl)CO <sub>2</sub> Et) (61)		865		95
Fe(TPP)(=C(Cl)CN) (62)		865		95
Fe(TPP)(=C(Cl)R) (R = Me, CHMe <sub>2</sub> ) (63a, 63b)				94
Fe(TPP)(=C(Cl)R) (R = CH <sub>2</sub> OH, CH(OH)Me, CH(OH)Ph, C(OH)Me <sub>2</sub> ) (64-67)				94
Fe(TPP)(=C(Cl)SR) (R = Ph, CH <sub>2</sub> Ph, phthalimido) (68a-c)				45, 96
Fe(TPP)(=C(Cl)SeCH <sub>2</sub> Ph) (69)				96
Fe(TPP)(=C(Br)CH <sub>2</sub> OH) (70)				94
RuCl <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (71)	1023		1979	23
RuBr <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (72)	1025		1980	74
[RuCl(=C(F)NMe <sub>2</sub> )(CN- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (73)	1038		2003	23
[RuCl(=C(F)NMe <sub>2</sub> )(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (74)			1982	55
RuCl <sub>2</sub> (=C(F)OMe)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (75)	1060		1973	23
RuCl <sub>2</sub> (=C(F)OCHMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (76)			1991	55
RuCl <sub>2</sub> (=C(F)OCH <sub>2</sub> CMe <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (77)			1982	77



TABLE III (Continued)

	$\nu(\text{CF}), \text{cm}^{-1}$	$\nu(\text{CCl}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	ref
RuBr <sub>2</sub> (=C(F)SEt)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (78)	1060, 1020		1995	74
OsCl <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (79)			(1948, 1928) <sup>e</sup>	77
[OsCl(=C(F)NMe <sub>2</sub> )(MeCN)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]SbF <sub>6</sub> (80)			1956	77
OsCl <sub>2</sub> (=C(F)S- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (81)			(1963, 1949) <sup>e</sup>	55
OsCl <sub>2</sub> (=C(F)SEt)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (82)			1975	77
RuCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (83)		795	1980	24
RuCl(SCN)(=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (84)		805	1960	57
[RuCl(=C(Cl)NMe <sub>2</sub> )(CN- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (85)		814	1990	24
[RuCl(=C(Cl)NMe <sub>2</sub> )(CO)(PMe <sub>2</sub> Ph) <sub>3</sub> ]ClO <sub>4</sub> (86)			1925	57
RuCl <sub>2</sub> (=C(Cl)NEt <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (87)		765	1970	57
RuCl <sub>2</sub> (=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (88)		784	1990	82a
[RuCl(=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ]SbF <sub>6</sub> (89)		791	2010, 2075	82a
RuCl <sub>2</sub> (=C(Cl)Ph)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (90)		810	2000	57
OsCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (91)		790	1950	57
OsCl <sub>2</sub> (=C(Cl)- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (92)		800	1957	83
OsCl <sub>2</sub> (=C(Cl)Ph)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (93)		820	1960	57
OsClBr(=C(Br)Ph)(CO)(PPh <sub>3</sub> ) <sub>2</sub> <sup>b</sup> (94)			(1985, 1970) <sup>e</sup>	57
RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (95)				93
RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> (96)		807		93
[RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(CO)] <sub>2</sub> (97)		860		93
IrCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (98)		820		25
[IrCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(MeCN)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (99)		850		57
IrCl <sub>3</sub> (=C(Cl)N(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (100)		810		57
IrCl <sub>3</sub> (C(Cl)SMe)(PPh <sub>3</sub> ) <sub>2</sub> (101)		820		57
[IrCl <sub>2</sub> (=C(Cl)C <sub>6</sub> H <sub>4</sub> PPh <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+b</sup> (102)			2075	75

<sup>a</sup>Data recorded as Nujol mull unless otherwise specified. <sup>b</sup>Compound characterized spectroscopically. <sup>c</sup>CH<sub>2</sub>Cl<sub>2</sub>. <sup>d</sup>Value for <sup>13</sup>C-substituted ligand. <sup>e</sup>Solid-state splitting. <sup>f</sup>Ether. <sup>g</sup>CH<sub>2</sub>ClCHCl<sub>2</sub>. <sup>h</sup>Hexane.

TABLE IV. <sup>13</sup>C and <sup>19</sup>F NMR Data for Halocarbene Complexes

	shift, <sup>a</sup> ppm	coupling const, Hz	solv	ref
<sup>13</sup> C Data for C(carbene)				
[CpMo(=CF <sub>2</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub> (1)	279.8	<sup>1</sup> J <sub>CF</sub> = 471	SO <sub>2</sub> (l)	73
[CpMo(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> )]SbF <sub>6</sub> (2)	264.1	<sup>1</sup> J <sub>CF</sub> = 392 <sup>2</sup> J <sub>CF</sub> = 100	SO <sub>2</sub> (l)	73
[CpFe(=C(Cl)Me)(CO)(PPh <sub>3</sub> )]BF <sub>4</sub> (60)	344.5		CDCl <sub>3</sub>	91
[CpFe(=CCl <sub>2</sub> )(CO) <sub>2</sub> ]BCl <sub>4</sub> (7)	319.5		CD <sub>2</sub> Cl <sub>2</sub>	31
Cr(=C(Cl)NMe <sub>2</sub> )(CO) <sub>5</sub> (38)	246.78		acetone- <i>d</i> <sub>6</sub>	88
Cr(=C(F)NEt <sub>2</sub> )(CO) <sub>5</sub> (34)	245.70	<sup>1</sup> J <sub>CF</sub> = 393	CD <sub>2</sub> Cl <sub>2</sub>	86
Cr(=C(Cl)NEt <sub>2</sub> )(CO) <sub>5</sub> (35)	244.26		acetone- <i>d</i> <sub>6</sub>	89
Cr(=C(Br)NEt <sub>2</sub> )(CO) <sub>5</sub> (36)	241.3		THF- <i>d</i> <sub>6</sub>	87
(CO) <sub>5</sub> Re-Re(=C(Cl)SiPh <sub>3</sub> )(CO) <sub>4</sub> (58)	324.70		CD <sub>2</sub> Cl <sub>2</sub>	90
Fe(TPP)(=C(Cl)CHMe <sub>2</sub> ) (63b)	324.0		CDCl <sub>3</sub>	94
Fe(TPP)(=C(Cl)CH(OH)Me) (65)	312.0		CDCl <sub>3</sub>	94
Fe(TPP)(=C(Cl)CH(OH)Ph) (66)	303.0		CDCl <sub>3</sub>	94
Fe(TPP)(=C(Cl)CH <sub>2</sub> OH) (64)	302.7		CDCl <sub>3</sub>	94
Fe(TPP)(=C(Cl)SPh) (68a)	288.5		CDCl <sub>3</sub>	96
Fe(TPP)(=C(Cl)SCH <sub>2</sub> Ph) (68b)	266.4		CDCl <sub>3</sub>	96
Fe(TPP)(=C(Cl)SeCH <sub>2</sub> Ph) (69)	265.1		CDCl <sub>3</sub>	96
Fe(TPP)(=C(Cl)SNC <sub>3</sub> H <sub>4</sub> O <sub>2</sub> ) (68c)	264.3		CDCl <sub>3</sub>	96
Fe(TPP)(=C(Cl)CO <sub>2</sub> Et) (61)	234.0		CDCl <sub>3</sub>	95
Fe(TPP)(=CCl <sub>2</sub> ) (13)	224.7		CDCl <sub>3</sub>	10
Fe(TPP)(=C(Cl)CN) (62)	210.0		CDCl <sub>3</sub>	95
[RuCl(=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]SbF <sub>6</sub> (89)	267.7		CDCl <sub>3</sub>	82b
RuCl <sub>2</sub> (=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (88)	256.85		CD <sub>2</sub> Cl <sub>2</sub>	82b
OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (21)	223.2	<sup>2</sup> J <sub>CP</sub> = 10	CDCl <sub>3</sub>	13
[RuCl(=C(Cl)NMe <sub>2</sub> )(CN- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (85)	222.28	<sup>2</sup> J <sub>CP</sub> = 9	CDCl <sub>3</sub>	57
<sup>19</sup> F NMR Data				
[CpMo(=CF <sub>2</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub> (1)	242.47 <sup>b</sup>		SO <sub>2</sub> (l)	73
[CpMo(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> )]SbF <sub>6</sub> (2)	239.04 <sup>b</sup>		SO <sub>2</sub> (l)	73
[CpMo(=C(F)C <sub>2</sub> F <sub>5</sub> )(CO) <sub>3</sub> ]SbF <sub>6</sub> (33)	185.03 <sup>b</sup> (CF)	<sup>3</sup> J <sub>FF</sub> = 16.1	SO <sub>2</sub> (l)	73
		<sup>4</sup> J <sub>FF</sub> = 8.0		
	-28.35 <sup>b</sup> (CF <sub>2</sub> )	<sup>3</sup> J <sub>FF</sub> = 16.1		
		<sup>3</sup> J <sub>FF</sub> = 2.4		
	-1.62 <sup>b</sup> (CF <sub>3</sub> )	<sup>4</sup> J <sub>FF</sub> = 8.0		
		<sup>3</sup> J <sub>FF</sub> = 2.4		
[CpFe(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> )]BF <sub>4</sub> (5)	164 <sup>c</sup>	<i>d</i>	CD <sub>2</sub> Cl <sub>2</sub>	32
[CpFe(=CFCl)(CO)(PPh <sub>3</sub> )] <sup>+</sup> (6)	207 <sup>c</sup>	<i>d</i>	CD <sub>2</sub> Cl <sub>2</sub>	32
Ir(=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (31)	75 <sup>c</sup>	<i>e</i>	CDCl <sub>3</sub>	37

<sup>a</sup>Shift vs TMS. <sup>b</sup>Shift vs external CF<sub>3</sub>CO<sub>2</sub>H. <sup>c</sup>Shift vs external CF<sub>3</sub>Cl. <sup>d</sup>Singlet due to rapid rotation about Fe=C bond. <sup>e</sup>Non-first-order coupling; *J* values not assigned.

analogous to proton data for alkylidene species  $L_nM=CHR$ , where the carbene proton is shifted downfield relative to the protons in the alkyl R group.<sup>7</sup>

The crystal structures of the two zerovalent osmium  $CF_2$  complexes and the  $d^8$  iridium(I)  $CF_2$  complex all demonstrated the vertical orientation of the  $CF_2$  ligand relative to the equatorial plane in these trigonal-bipyramidal structures. This conformation is retained in solution, as evidenced by room-temperature  $^{31}P$  NMR data for the two osmium complexes and for  $IrI(=CF_2)(CO)(PPh_3)_2$ .<sup>37</sup> In each case the phosphine resonance appears as a doublet of doublets ( $^3J_{PF} - 25$  Hz), indicating the presence of magnetically inequivalent pairs of F and P atoms. This requires that the orientation of the carbene ligand must be vertical and that rotation about the  $M=C$  bond must be slow on the NMR time scale, as either an in-plane orientation of the carbene or rapid rotation would result in a triplet for the phosphine resonance.<sup>37</sup> This contrasts with the results observed for  $[CpFe(=CF_2)(CO)(PPh_3)]BF_4$ , for which the  $^{19}F$  spectrum shows a singlet from  $-80$  to  $25$  °C, consistent with rapid rotation about the  $Fe=C$  bond over this temperature range.<sup>32</sup> Although the crystal structure of this complex shows that it adopts the predicted conformation in the solid state, the variable-temperature solution NMR data indicate that the barrier to rotation must be low.

## V. Reactivity

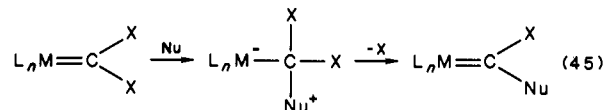
### A. Control of Metal Carbene Reactivity

The discussion of bonding in transition-metal carbene systems in section II indicates that for carbene fragments with a singlet ground state such as those under consideration here, the  $M=C$   $\pi$  orbital of a donor/acceptor double bond can be considered to arise from overlap of a filled metal d orbital with an empty carbon orbital of  $\pi$  symmetry, which is predominantly the C p orbital. The energy difference between the C and M orbitals participating in this bond results in an antibonding  $\pi^*$  orbital which is low-lying in energy and is largely localized on the carbene carbon atom. Several theoretical studies on the bonding in carbene complexes confirm that this orbital is the LUMO of the metal carbene complex.<sup>104,112,113</sup> The HOMO is a filled metal d orbital not associated with the metal-carbene bond.

The charge distribution within metal carbene complexes has been estimated by Mulliken population analysis.<sup>113,114</sup> The charge on the carbene carbon atom is usually negative and becomes more negative as the  $M-C$  interaction increases. The metal-carbon bond is polarized  $M^{\delta+}-C^{\delta-}$ , and the carbene carbon is more negative than the carbon of any carbonyl ligand in the complex. Finally, changing the charge on the complex from neutral to cationic renders the carbene carbon slightly positive.

The importance of either frontier orbital control or electronic charge control in the reactions of transition-metal organometallic species has been recognized.<sup>115</sup> Theoretical calculations indicate that addition of nucleophiles to metal carbene complexes is frontier orbital controlled rather than charge controlled. Although either the metal center or the carbene carbon atom are potential sites for nucleophilic attack, frontier orbital control directs the HOMO of the attacking nucleophile

toward the LUMO of the metal carbene complex, which is localized on the carbene carbon atom as described above. Population of the LUMO, the  $M-C$  antibonding  $\pi^*$  orbital, destroys the  $M-C$   $\pi$  interaction and forms an intermediate complex with a  $M-C$  single bond (eq 45). Ylide-type intermediates of this sort have been



proposed for nucleophilic substitution reactions in carbene complexes, and several highly electrophilic carbene complexes have been isolated as adducts with nucleophiles, supporting this mechanism.<sup>7,27</sup>

According to this scheme, nucleophilic attack will be facilitated when the nature of the metal complex and the carbene substituents result in a low-lying  $M-C$   $\pi^*$  orbital that is localized on the carbene carbon atom and when the negative charge on this atom is minimized. Heteroatom substituents provide for the former criterion, while the latter requires an electron-deficient metal center (the presence of good  $\pi$ -acceptor ligands or a cationic complex) and substituents on the carbene that are good electron-withdrawing groups but not good  $\pi$  donors. The charge distribution has been calculated specifically for a halocarbene complex in only one case and predicted that the carbene complex atom in  $Fe(TPP)(=CCl_2)$  should have a positively charged carbene carbon atom.<sup>116</sup> Thus dihalocarbene complexes containing a  $d^6$  metal center and ancillary ligands such as CO should be excellent substrates for nucleophilic attack at the carbene carbon atom. Furthermore, the good leaving-group characteristics of the halides means that the predominant outcome of nucleophilic attack is substitution, emphasizing the synthetic utility of the dihalocarbene ligands as precursors to other carbene species (eq 45). Nucleophilic substitutions comprise the most abundant class of reactions of dihalocarbene complexes.

This scheme also indicates that replacement of one halide substituent by a group with better  $\pi$ -donor characteristics such as OR, SR, or  $NR_2$  should stabilize the carbene ligand, rendering it less susceptible to nucleophilic attack. The presence of a more electron-rich metal center should have a similar result. The chemistry of the monohalocarbene species and the zerovalent ruthenium and osmium dihalocarbene complexes outlined below illustrates these points.

As the  $M=C$  bonding interaction moves from donor/acceptor type bonding, with frontier orbital control of bonding as described above, toward covalent bonding, the  $\pi^*$  orbital is raised in energy and also becomes delocalized so that it is no longer significantly localized on the carbene carbon atom. As a result this orbital is no longer the LUMO. The new LUMO of the complex will be an orbital that is not associated with the metal-carbon bond.<sup>113</sup> The reactivity alters, too, so that nucleophilic substitution at the carbene ligand no longer predominates, and the complex becomes susceptible to attack by electrophiles. Since the LUMO is no longer associated with the metal-carbon bond the reactivity is charge controlled. Experimentally, there are two possible sites for electrophilic attack: the metal center or the negatively charged carbene carbon atom. Reactions of this sort will be favored when the metal

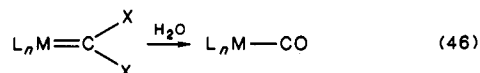
center is electron-rich, with ancillary ligands which are electron-releasing, and when the carbene substituents are poor  $\pi$  donors, as in the alkyl substituents of alkyldiene complexes.

The substitution reactions are tabulated according to metal complex in Table V for easy reference but are discussed below according to the nature of the attacking nucleophile.

## B. Electrophilic Reactivity at the Carbene Carbon

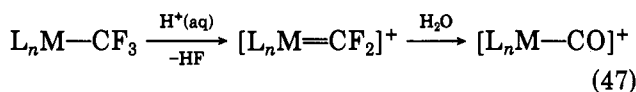
### 1. Nucleophilic Substitution Reactions

**a. Group 16 Nucleophiles (O, S, Se, Te).** A reaction common to most electrophilic dihalocarbene complexes is hydrolysis of the  $CX_2$  ligand to a CO ligand (eq 46). The hydrolysis reaction has been reported for



the Mo complexes **1** and **27**<sup>3</sup> and for the groups 8 and 9  $d^6$  species **4**, **5**, **7**,<sup>31</sup> **15**,<sup>23</sup> **19**, **21**,<sup>13,24</sup> and **25**<sup>25</sup> and is presumably general for this class of compounds. The facility with which this reaction proceeds gives an insight into the relative stability and electrophilicity of the dihalocarbene complexes. For example, in the preparation of  $L_nM=CF_2$  complexes by  $SbF_5$ -mediated fluoride abstraction from the  $CF_3$  species, a number of substrates gave CO complexes, indicating that the extreme moisture sensitivity of the possible  $M=CF_2$  intermediates has precluded isolation or observation of the complexes.<sup>73</sup> At the other extreme, the zerovalent Ru and Os species  $M(=CF_2)(CO)_2(PPh_3)_2$  hydrolyze only very slowly, indicating the much reduced electrophilicity at the carbene carbon.<sup>6,7,76</sup>

Hydrolysis reactions of  $[CpFe(=CX_2)(CO)L]^+$  ( $X = F, Cl$ ;  $L = CO, PPh_3$ ) and the  $CX_3$  precursors both yielded the complexes  $[CpFe(CO)_2L]^+$ , indicating that these and other  $M-CX_3$  complexes may hydrolyze via  $M=CX_2$  intermediates (eq 47).<sup>31</sup> The reactivity of

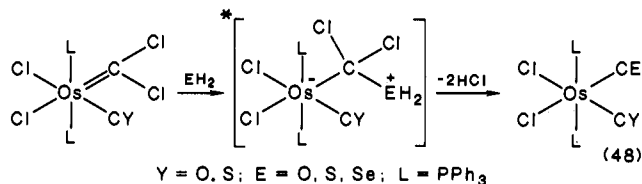


$CpFe(CX_3)(CO)_2$  toward nucleophiles is in the order  $F < Cl < Br < I$ , which parallels the order of accessibility of the dihalocarbene intermediate. A further reaction of  $[CpFe(=CCl_2)(CO)_2]^+$  is capture of chloride from  $[PPN]Cl$  to form the  $Fe-CCl_3$  complex. This trichloromethyl species is also observed to form from slow decomposition of the dichlorocarbene complex in solution.<sup>31,71,72</sup> Again, this may arise from capture of chloride released during hydrolytic decomposition.

The heavier chalcogenide analogue of hydrolysis is observed for the Ru and Os dichlorocarbene complexes **19**, **21**, and **23** which react with  $H_2E$  ( $E = O, S, Se$ ) to give the chalcocarbonyl complexes  $L_nM-CE$ . Reaction of **21** with  $EH^-$  ( $E = O, S, Se, Te$ ) produced the first complete series of chalcocarbonyl complexes, including the first CTe complex. The CS, CSe, and CTe complexes were characterized by X-ray crystallography.<sup>13</sup> In general, the reactivity of the osmium complexes **21** and **23**,  $OsCl_2(=CCl_2)(CE)(PPh_3)_2$  ( $E = O, S$ ), is very similar except that the CS ligand of **23** competes with the  $CCl_2$  ligand for some nucleophiles. For example,

no chalcocarbonyl products are observed in the reaction of **23** with  $EH^-$  ( $E = S, Se, Te$ ).<sup>13</sup> The Ir complex **25** reacts with  $H_2S$  or  $SH^-$  to give a thiocarbonyl product.<sup>25</sup>

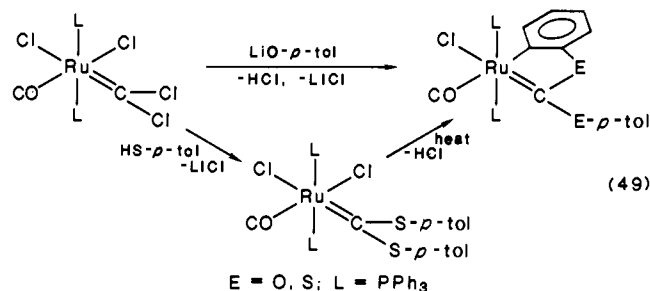
The mechanism of chalcocarbonyl formation is unknown but may involve formation of an ylide intermediate and subsequent double loss of HCl (eq 48).<sup>13</sup>



Ylide-like complexes similar to the proposed intermediate have been reported,<sup>117</sup> and a further comparison is the iron porphyrin complexes  $Fe(TPP)(=C(Cl)-ECH_2Ph)$  ( $E = S, Se$ ) which lose  $PhCH_2Cl$  to form  $Fe(TPP)CE$ .<sup>96</sup> The same species can be formed directly from  $Fe(TPP)$  and  $Cl_3CECH_2Ph$  with iron powder as a reductant<sup>96</sup> or by nucleophilic attack of  $EH^-$  on  $Fe(TPP)(=CCl_2)$ .<sup>118</sup>

Reactions of dihalocarbene complexes with alcohols or thiols occur under mild conditions and in general lead to substitution of one halide moiety to give monohalocarbene complexes. Occasionally, substitution of both halides may occur. The rate of reaction of  $RuCl_2(=CF_2)(CO)(PPh_3)_2$  (**15**) with ROH to give  $RuCl_2(=C(F)OR)(CO)(PPh_3)_2$  follows the order  $R = Me > CHMe_2 > CH_2CMe_3$ , which suggests that steric factors are important in the substitution reaction. The complex with  $R = CH_2CMe_3$  is one of the few monohalocarbene species to be characterized structurally.<sup>23,55,77</sup> Substitution of both fluorides occurs upon reaction of **15** with 1,2-ethanediol, producing a dioxanylidene complex. In this case entropic reasons may favor cyclization of a fluoroalkoxy intermediate.<sup>23</sup>

In contrast, the dichlorocarbene analogue of compound **15**,  $RuCl_2(=CCl_2)(CO)Ph_3$  (**19**), does not react with simple alcohols, and this species can be recrystallized from EtOH solution. Reaction of **19** with catechol gives the cyclic dialkoxy carbene product, but reaction with *p*-cresol only occurs if the preformed Li salt,  $LiO-p-tol$ , is used. The product results from disubstitution followed by *ortho*-metalation of one aromatic carbene substituent (eq 49). Evidence for the



intermediacy of the simple carbene complex  $L_nRu=C(O-p-tol)_2$  comes from a comparison of the reaction with the sulfur analogue. Reaction of **19** with *p*-toluenethiol gives the simple carbene  $L_nRu=C(S-p-tol)_2$ , and subsequent heating of this complex results in the *ortho*-metalated product.<sup>24</sup>

Double substitution occurs when the Ru complex **19** is treated with methanethiol,<sup>24</sup> in contrast to the reaction of the Ir dichlorocarbene **25**, which undergoes only a single substitution to give a chlorothiocabene com-

TABLE V. Reactions of Electrophilic Carbene Centers with Nucleophiles

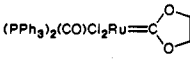
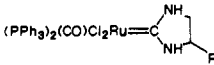
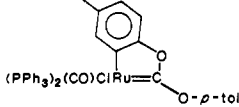
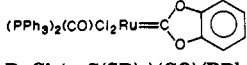
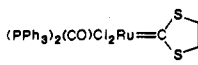
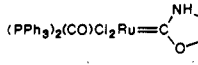
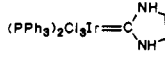
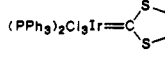
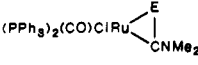
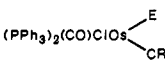
substrate	nucleophile		product	ref
Dihalocarbene Complexes				
[CpMo(=CF <sub>2</sub> )(CO)L]SbF <sub>6</sub> (1, 2)	L = CO, PPh <sub>3</sub>	H <sub>2</sub> O	[CpMo(CO) <sub>2</sub> L] <sup>+</sup>	73
[Mn(=CF <sub>2</sub> )(CO) <sub>5</sub> ]BF <sub>4</sub> (3)		H <sub>2</sub> O	[Mn(CO) <sub>5</sub> ] <sup>+</sup> a	31
[CpFe(=CF <sub>2</sub> )(CO)L]BF <sub>4</sub> (4, 5)	L = CO, PPh <sub>3</sub>	H <sub>2</sub> O	[CpFe(CO) <sub>2</sub> L] <sup>+</sup> a	31
4	L = CO	IrCl(CO)L' <sub>2</sub>	[Cp(CO)Fe(μ-CF <sub>2</sub> )(μ-CO)- IrCl(CO)L' <sub>2</sub> ]BF <sub>4</sub> (111)	121
[CpFe(=CCl <sub>2</sub> )(CO) <sub>2</sub> ] <sup>+</sup> (7)		H <sub>2</sub> O NH <sub>3</sub>	[CpFe(CO) <sub>3</sub> ] <sup>+</sup> a CpFe(CN)(CO) <sub>2</sub>	31 31, 71, 72
		<sup>i</sup> PrNH <sub>2</sub> [PPn]Cl	[CpFe(CN <sup>i</sup> Pr)(CO) <sub>2</sub> ] <sup>+</sup> CpFe(CCl <sub>3</sub> )(CO) <sub>2</sub>	31 31, 71, 72
Fe(TPP)(=CCl <sub>2</sub> ) (13)		RNH <sub>2</sub>	Fe(TPP)(CNR)(RNH <sub>2</sub> )	10, 119, 45, 79
		R = <sup>n</sup> Bu, <sup>i</sup> Pr, <sup>t</sup> Bu, Ph, cyclohexyl		
		E = S, Se	Fe(TPP)(CE)	118
RuCl <sub>2</sub> (=CF <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (15)		NaEH H <sub>2</sub> O MeNH <sub>2</sub> Me <sub>2</sub> NH ROH	RuCl <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> RuCl <sub>2</sub> (CNMe)(CO)(PPh <sub>3</sub> ) <sub>2</sub> RuCl <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (71) RuCl <sub>2</sub> (=C(F)OR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (75)	23 55 23 23
		R = Me R = CHMe <sub>2</sub> R = CH <sub>2</sub> CMe <sub>3</sub>	76 77	55 77
		HOCH <sub>2</sub> CH <sub>2</sub> OH		23
RuBr <sub>2</sub> (=CFBr)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (16)		Me <sub>2</sub> NH EtSH	RuBr <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (72) RuBr <sub>2</sub> (=C(F)SEt)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (78)	74 74
OsCl <sub>2</sub> (=CFCl)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (17)		H <sub>2</sub> O Me <sub>2</sub> NH RSH NaSR	OsCl <sub>2</sub> (CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> OsCl <sub>2</sub> (=C(F)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (79) OsCl <sub>2</sub> (=C(F)SR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (81)	55 57 77
		R = <i>p</i> -tol R = Et	82	
[OsCl(=CFCl)(MeCN)(CO)- (PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (18)		Me <sub>2</sub> NH	[OsCl(=C(F)NMe <sub>2</sub> )(MeCN)- (CO)(PPh <sub>3</sub> ) <sub>2</sub> ]ClO <sub>4</sub> (80)	77
MCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (19, 21)	M = Ru, Os M = Os M = Ru, Os M = Ru M = Ru M = Os	H <sub>2</sub> E NaEH RNH <sub>2</sub> R <sub>2</sub> NH	MCl <sub>2</sub> (CE)(CO)(PPh <sub>3</sub> ) <sub>2</sub> OsCl <sub>2</sub> (CE)(CO)(PPh <sub>3</sub> ) <sub>2</sub> MCl <sub>2</sub> (CNR)(CO)(PPh <sub>3</sub> ) <sub>2</sub> MCl <sub>2</sub> (=C(Cl)NR <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (83)	13, 24 13 13, 24 24
		E = O, S, Se E = O, S, Se, Te R = Me, <i>p</i> -tol R = Me R = Et R = Me	87 91	57 57
RuCl <sub>2</sub> (=CCl <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (19)		NH <sub>3</sub> Me <sub>2</sub> NNH <sub>2</sub> H <sub>2</sub> NCHRCH <sub>2</sub> NH <sub>2</sub>	RuCl(CN)(NH <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> RuCl <sub>2</sub> (CNNMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	24 24
		R = H, Me		24
		LiO- <i>p</i> -tol		24
		catechol		24
		RSH	RuCl <sub>2</sub> (=C(SR) <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	24
		R = Me, Et, <i>p</i> -tol		
		HSCH <sub>2</sub> CH <sub>2</sub> SH		24
		H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> OH		24
OsCl <sub>2</sub> (=CCl <sub>2</sub> )(CS)(PPh <sub>3</sub> ) <sub>2</sub> (23)		H <sub>2</sub> E	OsCl <sub>2</sub> (CE)(CS)(PPh <sub>3</sub> ) <sub>2</sub>	13
IrCl <sub>3</sub> (=CCl <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (25)		H <sub>2</sub> E MeNH <sub>2</sub> Me <sub>2</sub> NH HN(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	IrCl <sub>3</sub> (CE)(PPh <sub>3</sub> ) <sub>2</sub> IrCl <sub>3</sub> (CNMe)(PPh <sub>3</sub> ) <sub>2</sub> IrCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (98) IrCl <sub>3</sub> (=C(Cl)N(CH <sub>2</sub> ) <sub>4</sub> CH <sub>2</sub> )- (PPh <sub>3</sub> ) <sub>2</sub> (100)	25 25 25 57
		E = O, S, Se E = O, S		
		H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>		25
		HS <sup>-</sup> HSM <sub>e</sub>	IrCl <sub>3</sub> (CS)(PPh <sub>3</sub> ) <sub>2</sub> IrCl <sub>3</sub> (=C(Cl)SMe)(PPh <sub>3</sub> ) <sub>2</sub> (101)	57 57
		HSCH <sub>2</sub> CH <sub>2</sub> SH		25
M(=CF <sub>2</sub> )(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub> (26, 27)	M = Ru, Os	H <sub>2</sub> O	M(CO) <sub>3</sub> (PPh <sub>3</sub> ) <sub>2</sub>	76
Ru(=CF <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> (26)		MeNH <sub>2</sub> H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>	Ru(CNMe)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> Ru(CNCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub> )(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> <sup>a</sup>	76 55

TABLE V (Continued)

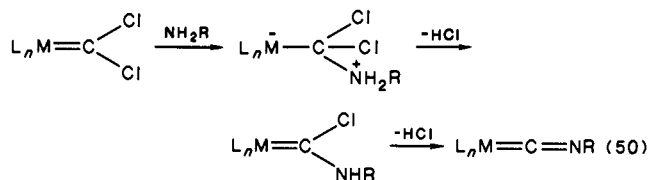
substrate	nucleophile	product	ref
Monohalocarbene Complexes			
Cr(=C(Cl)NMe <sub>2</sub> )(CO) <sub>5</sub> (38)	KCN	Cr(=C(CN)NMe <sub>2</sub> )(CO) <sub>5</sub>	82b
[CpMo(=C(F)CF <sub>3</sub> )(CO) <sub>3</sub> ] <sup>+</sup> <sup>b</sup>	H <sub>2</sub> O/H <sup>+</sup>	CpMo(C(O)CF <sub>3</sub> )(CO) <sub>3</sub>	31
(CO) <sub>5</sub> Re—Re(=C(X)SiPh <sub>3</sub> )(CO) <sub>4</sub> (58, 59)	X = Cl, Br ROH	(CO) <sub>5</sub> Re—Re(=C(OR)SiPh <sub>3</sub> )(CO) <sub>4</sub>	90
[CpFe(=C(Cl)CH <sub>3</sub> )(CO)- (PPh <sub>3</sub> ) <sub>2</sub> BF <sub>4</sub> (60)]	H <sub>2</sub> O	CpFe(C(O)CH <sub>3</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	91
Fe(TPP)(=C(Cl)R) (63)	R = Me, MeOH R = Me, EtOH R = Me, PhCH <sub>2</sub> SH	Fe(TPP)(=C(OMe)R) Fe(TPP)(=C(OEt)Me) Fe(TPP)(=C(SCH <sub>2</sub> Ph)Me)	94
RuCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (83)	NaEH	(PPh <sub>3</sub> ) <sub>2</sub> (CO)ClRu 	24
	NaHFe(CO) <sub>4</sub> / EtOH	RuCl <sub>2</sub> (=C(H)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	57
OsCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (91)	NaBH <sub>4</sub>	OsCl <sub>2</sub> (=C(H)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>	57
OsCl <sub>2</sub> (=C(Cl)R)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (92, 93)	R = <i>p</i> -tol H <sub>2</sub> O	OsCl(R)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	83
	R = <i>p</i> -tol NaEH	(PPh <sub>3</sub> ) <sub>2</sub> (CO)ClOs 	83
	R = <i>p</i> -tol LiEt <sub>3</sub> H	OsCl <sub>2</sub> (=CHR)(CO)(PPh <sub>3</sub> ) <sub>2</sub>	83
	R = <i>p</i> -tol R'NH <sub>2</sub>	OsCl <sub>2</sub> (=C(R)NHR')(CO)(PPh <sub>3</sub> ) <sub>2</sub>	83
	R = Ph R'SH	OsCl <sub>2</sub> (=C(R)SR')(CO)(PPh <sub>3</sub> ) <sub>2</sub>	57

<sup>a</sup> Product characterized spectroscopically. <sup>b</sup> Presumed intermediate in hydrolysis of CpMo(CF<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>.

plex.<sup>25</sup> Both complexes produce the cyclic dithiocarbene species upon reaction with 1,2-ethanethiol.<sup>24,25</sup> Reaction of the mixed dihalocarbene complexes L<sub>n</sub>Ru=CFBr (16) and L<sub>n</sub>Os=CFCl (17) with thiols or thiolates in each case produces the fluorothiocarbene product, reflecting the better leaving group properties of Cl or Br relative to F.<sup>55,74,77</sup>

**b. Nitrogen Nucleophiles.** The simplest nitrogen-based nucleophile available is ammonia, and this transforms the dichlorocarbene ligand in 19 to a cyano ligand, producing RuCl(CN)(NH<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>.<sup>24</sup> Similarly, ammonolysis of the cationic dichlorocarbene complex [CpFe(=CCl<sub>2</sub>)(CO)<sub>2</sub>]<sup>+</sup> yields CpFe(CN)-(CO)<sub>2</sub>.<sup>31</sup>

Perhaps the most general reaction of electrophilic dihalocarbene complexes is with primary amines, resulting in products containing isocyanide ligands (eq 50). This transformation is observed for most of the



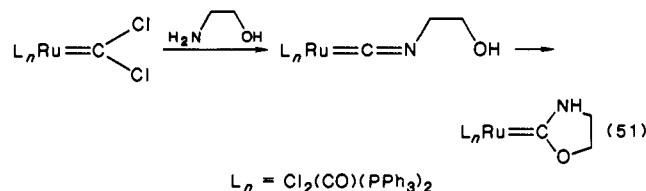
d<sup>6</sup> dihalocarbene complexes including 7,<sup>31</sup> 13,<sup>10,45,79,119</sup> 15,<sup>23</sup> 19,<sup>24</sup> 21,<sup>13</sup> and 25,<sup>25</sup> with both alkyl and aryl RNH<sub>2</sub>. The mechanism of isocyanide formation may, like the hydrolysis reaction, involve successive HCl loss from an ylide intermediate. This mechanism has been inferred from a detailed study of aminolysis reactions of group 6 heterocarbene complexes.<sup>120</sup>

The rate may correlate with the steric bulk of the R group as evidenced by the order of reactivity R = *n*-Bu > *i*-Pr > *t*-Bu, for the reaction of RNH<sub>2</sub> with Fe(TPP)(=CCl<sub>2</sub>) (13).<sup>119a</sup> A further kinetic study established two competing processes for this reaction.<sup>119b</sup> The first, involving *n*-alkylamines and leading predominantly to Fe(TPP)(CNR)(RNH<sub>2</sub>), arises from nucleophilic attack at the carbene carbon as outlined above. The second, leading to mixtures of the isocyanide

product and Fe(TPP)(RNH<sub>2</sub>)<sub>2</sub>, correlated with more sterically hindered or weakly basic amines (*t*-BuNH<sub>2</sub>, PhNH<sub>2</sub>) and was proposed to occur via a dissociative pathway, independent of the nature of the amine, involving initial loss of the CCl<sub>2</sub> ligand. Although this may be a kinetically sound mechanism, chemically there is little evidence or precedent for dissociative loss of a :CCl<sub>2</sub> fragment as proposed in this study.<sup>119b</sup>

Finally, the reaction has been suggested as a convenient route for the preparation of isotopically labeled isocyanides, \*CNR, using \*CCl<sub>4</sub> as the source of the \*CCl<sub>2</sub> ligand. More powerful nucleophiles (PPh<sub>3</sub>, RS<sup>-</sup>) completely destroy the carbene ligand in complex 13.<sup>119a</sup>

The isocyanide-forming reaction is general even for more complex amines. A (dimethylamino)isocyanide complex L<sub>n</sub>Ru=CNNMe<sub>2</sub> results when 19 is treated with dimethylhydrazine, H<sub>2</sub>NNMe<sub>2</sub>.<sup>24</sup> However, neither 19 nor 25 produce an isocyanide complex upon reaction with ethylenediamine but rather the cyclic diamino-carbene complex results.<sup>24,25</sup> The reaction may proceed via initial formation of an isocyanide species, L<sub>n</sub>M=CNCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, followed by intramolecular nucleophilic attack by the pendant amino function at the isocyanide carbon. Evidence for this proposal comes from the reaction of 19 with ethanolamine at ambient temperature. Rapid workup results in isolation of the isocyanide complex, but upon slow recrystallization cyclization occurs to form the aminoalkoxycarbene complex (eq 51).<sup>24</sup> This result also indicates clearly the relative reactivity of amine and alcohol nucleophiles toward the =CCl<sub>2</sub> ligand.



The much less electrophilic zerovalent complex Ru(=CF<sub>2</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (26) is unreactive toward alcohol but does react with MeNH<sub>2</sub> to form the air-sensitive



zerovalent Ru=C(NMe) complex.<sup>76</sup> However, reaction of **26** with ethylenediamine produces the isocyanide complex Ru=C(NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>) rather than the cyclic carbene complex observed for the ruthenium(II) precursor.<sup>55</sup> The isocyanide ligand is a good  $\pi$  acceptor and is more suited to the electron-rich metal center than the diaminocarbene ligand with its  $\pi$ -donor substituents.

The reaction of the dihalocarbene ligand with primary amines to produce an isocyanide ligand is complemented by the reaction with secondary amines, R<sub>2</sub>NH, to produce a haloaminocarbene ligand. Again, this reaction is general for the d<sup>6</sup> complexes, with compounds **15**,<sup>23</sup> **16**,<sup>74</sup> **17**, and **18**<sup>57,77</sup> leading to fluoroaminocarbene complexes, and compounds **19**,<sup>24</sup> **21**,<sup>13</sup> and **25**<sup>25</sup> giving chloroaminocarbenes. These complexes join a number of other haloaminocarbene species produced by a variety of complementary synthetic routes, as outlined in the synthesis section.

**c. Carbon Nucleophiles.** The reaction of the iridium dichlorocarbene complex **25** with the saturated nitrogen heterocycle piperidine produced a chloroaminocarbene complex.<sup>57</sup> The different reactivity of an aromatic nitrogen heterocycle is evidenced by the reaction of RuCl<sub>2</sub>(=C(Cl)<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**19**) with pyrrole. Substitution of one chloro ligand in the complex does occur, but the product is not the N-bound but rather the C-bound 2-pyrrolylchlorocarbene complex. Preliminary results indicate that this complex has a rich chemistry with nucleophiles.<sup>82a</sup>

Addition of aryllithium reagents to the osmium dichlorocarbene complex **21** does not give a simple substitution reaction but rather results in the zerovalent osmium carbyne complex OsCl(=CR)(CO)(PPh<sub>3</sub>)<sub>2</sub>.<sup>83</sup> This chemistry will be described in more detail below.

**d. Metal Nucleophiles.** In two examples an electrophilic dihalocarbene complex reacts with a nucleophilic metal center. In the first, treatment of [CpFe(=CF<sub>2</sub>)(CO)<sub>2</sub>]BF<sub>4</sub> with the electron-rich iridium complex IrCl(CO)(PMe<sub>2</sub>Ph)<sub>2</sub> results in formation of a bond between the Ir atom and the intact CF<sub>2</sub> fragment. The structurally characterized product is [CpFe(CO)( $\mu$ -CF<sub>2</sub>)( $\mu$ -CO)IrCl(CO)(PMe<sub>2</sub>Ph)<sub>2</sub>]BF<sub>4</sub>.<sup>121</sup> This reaction and the dinuclear product will be discussed in more detail in section VI.

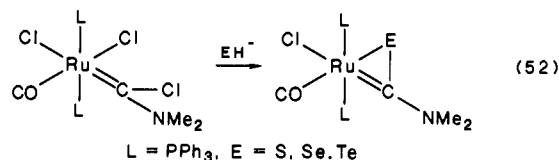
The iodo analogue of the iron porphyrin complex Fe(TPP)(=C(Cl)<sub>2</sub>) is implicated in the reaction of Fe(TPP) with Cl<sub>4</sub> under reducing conditions. However, the diiodocarbene complex is not isolated but is presumed to attack another molecule of Fe(TPP), which effectively replaces the iodo substituents, resulting in the  $\mu$ -carbido complex (TPP)Fe=C=Fe(TPP), as shown previously in eq 30.<sup>80</sup>

**e. Nucleophilic Attack on Monohalocarbene Complexes.** Replacement of one halide substituent in M=CX<sub>2</sub> by a good  $\pi$ -donor group such as NR<sub>2</sub>, OR, or SR reduces the electrophilicity of the carbene carbon sufficiently that very few monohalocarbene complexes are reactive toward substitution of the remaining halide. Exceptions are the few examples of double substitution and metallacycle formation driven by entropic factors described above and the examples described below. In general most complexes of the form L<sub>n</sub>M=C(X)Nu are stable with respect to hydrolysis and related reactions.

The chromium species Cr(=C(CN)NMe<sub>2</sub>)(CO)<sub>5</sub> is produced by reaction of the chloroaminocarbene com-

plex **38** with KCN. However, the same product can be prepared by CN<sup>-</sup> attack on the carbyne complex [Cr(=CNMe<sub>2</sub>)(CO)<sub>5</sub>]<sup>+</sup>, which is itself produced from the chloroaminocarbene complex **38**.<sup>82b</sup> This suggests that the carbyne complex may be an intermediate in the transformation of the chloroaminocarbene species to the cyanoaminocarbene product. Other facile interconversions of chloroaminocarbene and aminocarbene complexes have been reported.<sup>82b,84,88,122</sup>

Substitution of chloride in the chloroaminocarbene complex RuCl<sub>2</sub>(=C(Cl)NMe<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> (**83**) by the powerful nucleophiles EH<sup>-</sup> (E = S, Se, Te) with concomitant HCl elimination produces the  $\eta^2$ -chalcocarboxamido species shown in eq 52.<sup>24</sup> The ruthenium



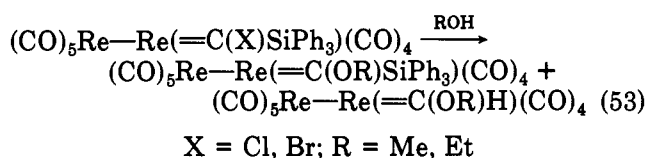
complex **83** and the osmium analogue **91** are subject to hydride attack using the reagents NaBH<sub>4</sub> and NaH-Fe(CO)<sub>4</sub>/EtOH, respectively, resulting in the aminocarbene complexes L<sub>n</sub>M=C(H)NMe<sub>2</sub>.<sup>57</sup>

The effect of the carbene substituent on reactivity toward nucleophiles is illustrated for a series of iron porphyrin monochlorocarbene complexes. There are two ways in which a nucleophile may interact with a five-coordinate metalloporphyrin carbene species, namely, coordination to the metal in the vacant axial site or attack at the carbene carbon atom. For example, both occur in the transformation of Fe(TPP)(=C(Cl)<sub>2</sub>) to Fe(TPP)(CNR)(RNH<sub>2</sub>) upon reaction with RNH<sub>2</sub>.<sup>10,45,79,119</sup> The monochlorocarbenes Fe(TPP)(=C(Cl)R) where R is CN or CO<sub>2</sub>Et have very high affinities for a sixth ligand in order to offset the effect of the strongly electron-withdrawing substituents on the carbene ligand. These same substituents, however, also render the carbene ligand more susceptible to nucleophilic displacement at the metal center. To some extent, the electron-rich porphyrin ligand must play a role in stabilizing the very electrophilic carbene carbon. These highly air-sensitive complexes will bind weakly coordinating ligands like DMF, THF, or MeOH, but interaction with the more nucleophilic pyridine results in immediate cleavage of the Fe-C bond.<sup>45</sup>

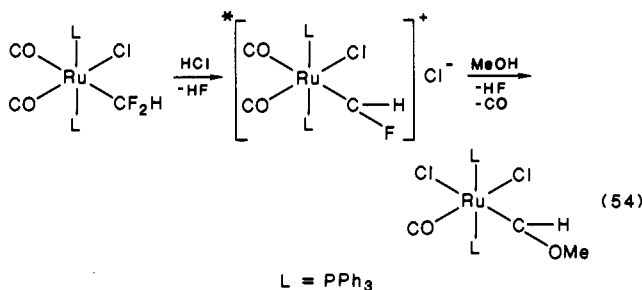
The opposite polarity of the complexes where R is an aliphatic group is evidenced by the much lower affinities for added donor ligands and a variable sensitivity toward oxygen.<sup>94</sup> This is also evident from the reactivity of these complexes toward alcohols and thiols, producing new carbene complexes, Fe(TPP)(=C(ER')R) from Fe(TPP)(=C(Cl)R) (R = Me, ER' = OMe, OEt, SCH<sub>2</sub>Ph; R = CHMe<sub>2</sub>, ER' = OMe). This reaction does not occur when R = CN, CO<sub>2</sub>Et, or Cl, illustrating the sensitivity of substitution reactions on monohalocarbenes toward the nature of the second substituent.<sup>94b</sup>

The monohalocarbene complexes L<sub>n</sub>M=C(X)R where the second substituent, R, is not a good  $\pi$  donor are quite susceptible to hydrolysis or alcoholysis. Acyl species L<sub>n</sub>M-C(O)R result from hydrolysis of the cationic species [CpFe(=C(Cl)Me)(CO)(PPh<sub>3</sub>)]<sup>+91</sup> and [CpMo(=C(F)CF<sub>3</sub>)(CO)<sub>3</sub>]<sup>3</sup>. The latter species is presumed to be the intermediate in the acid-promoted hydrolysis of CpMo(CF<sub>2</sub>CF<sub>3</sub>)(CO)<sub>3</sub>.<sup>31</sup> The reaction of (52)

the novel rhenium chloro(triphenylsilyl)carbene species with alcohol is shown in eq 53.<sup>90</sup>



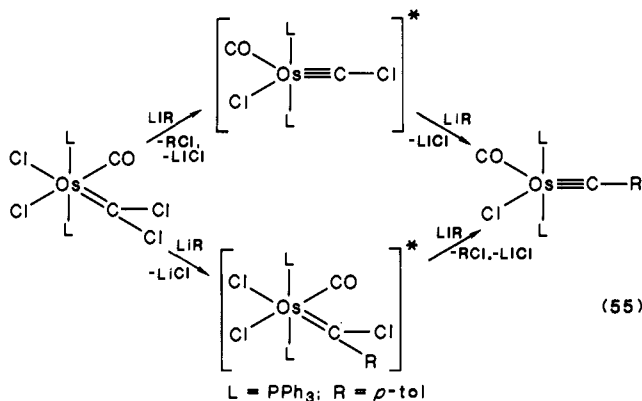
A highly reactive cationic ruthenium species containing the CHF carbene ligand is implicated when a fluoride substituent is abstracted from the CHF<sub>2</sub> ligand, as shown in eq 54.<sup>76</sup> The methoxycarbene product is formed by trapping of the carbene ligand in the highly reactive intermediate by MeOH attack on the fluoride substituent.



The haloarylcabene complex OsCl<sub>2</sub>(=C(Cl)*p*-tol)(CO)(PPh<sub>3</sub>)<sub>2</sub> is again without a stabilizing π-donor substituent on the carbene ligand and reacts with a variety of nucleophiles. The carbene complex is formed by Cl<sub>2</sub> addition to the zerovalent carbyne complex OsCl(≡C-*p*-tol)(CO)(PPh<sub>3</sub>)<sub>2</sub>, which itself reacts with electrophiles, and is prepared from the Os(II) dichlorocarbene complex 21. The relationship between these species and the reactions of the chloroarylcabene complex with nucleophiles is shown in Scheme II.<sup>57,83</sup>

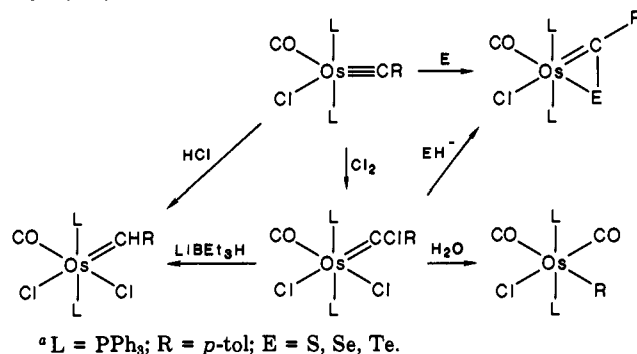
## 2. Metal Carbyne Formation

When OsCl<sub>2</sub>(=CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> is treated with *p*-tolyllithium, the result is the zerovalent carbyne complex OsCl(≡C-*p*-tol)(CO)(PPh<sub>3</sub>)<sub>2</sub>.<sup>83</sup> Of the two mechanisms which can be conceived for this reaction, shown in eq 55, it is thought that simple substitution of Cl by



the *p*-tolyl group to give the chloroarylcabene intermediate is not likely, as the independently prepared osmium C(Cl)-*p*-tol complex does not react with Li-*p*-tol to produce the carbyne species. There is no direct evidence for the chlorocarbyne intermediate shown in the other path. There is one example of a molybdenum chlorocarbyne complex, which will be described in a later section.

## SCHEME II<sup>a</sup>

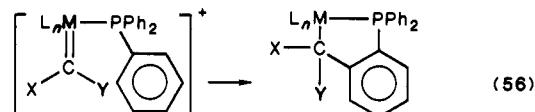


Use of an aryllithium species as nucleophile results in both substitution of the chlorides and formal reduction of the metal center and in this sense is different from all the other examples of electrophilic reactivity of dihalocarbene species considered above, where substitution occurs with no formal change in oxidation state of the metal center.

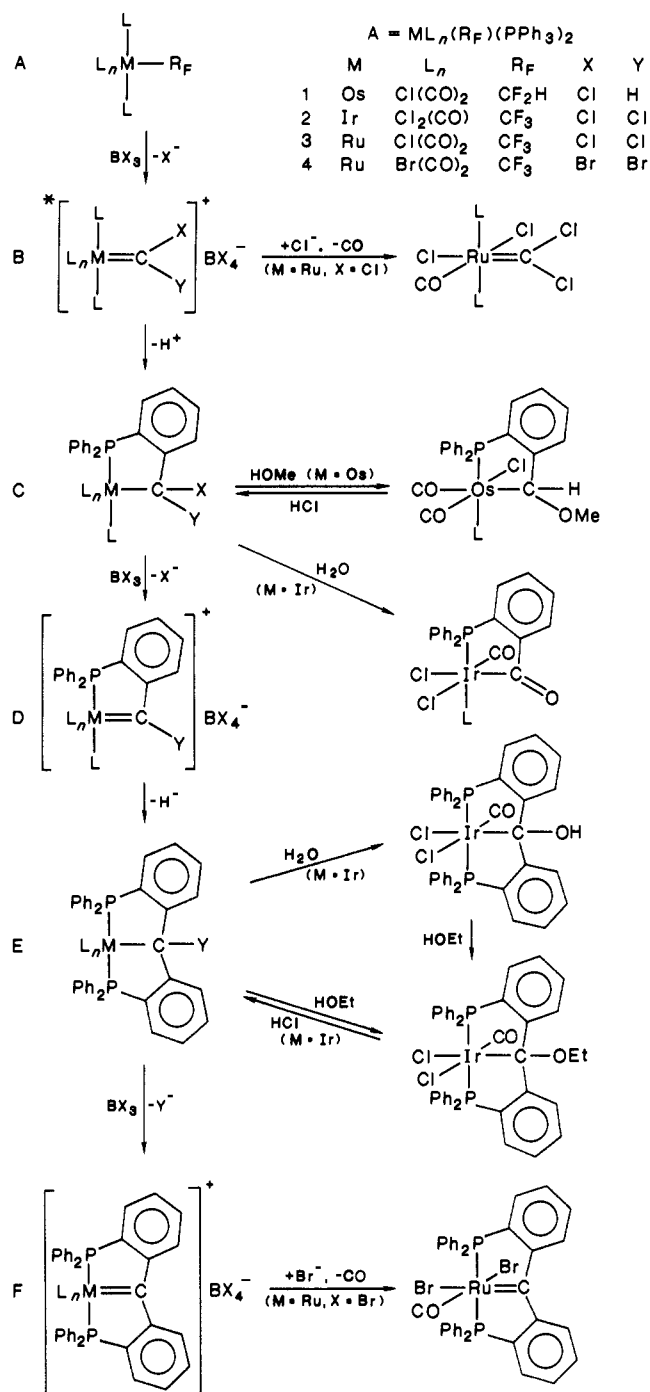
The zerovalent osmium carbyne complex itself is nucleophilic at the carbyne carbon. Reactions of this complex with electrophiles and the reactions of the chloroarylcabene complex with nucleophiles are complementary and are shown in the Scheme II.<sup>83</sup>

## 3. Electrophilic Aromatic Substitution

Substitution of a carbene Cl substituent in RuCl<sub>2</sub>(=C(Cl)*p*-tol)(CO)(PPh<sub>3</sub>)<sub>2</sub> by pyrrole to give the chloro-2-pyrrolylcabene complex can be regarded as an example of intermolecular electrophilic aromatic substitution by the electrophilic carbene center.<sup>82</sup> If the carbene ligand is sufficiently electrophilic, then the phenyl rings of the PPh<sub>3</sub> ligands may serve as substrates for intramolecular S<sub>E</sub>Ar, resulting in a metallacyclic product (eq 56).



The use of the boron trihalides for halide exchange of CF<sub>3</sub> ligands leading to CX<sub>3</sub> or CX<sub>2</sub> complexes was developed by Shriver and co-workers and was discussed in section III.<sup>31,32,71,72</sup> Attempts to repeat this procedure for other group 8 and 9 fluoromethyl complexes were successful only in the transformation of RuCl(CF<sub>3</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> to RuCl<sub>2</sub>(=CCl<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>, using BCl<sub>3</sub>.<sup>24</sup> This reaction was presumed to involve a cationic intermediate, denoted B\* in Scheme III. For the other ruthenium, osmium, or iridium CF<sub>3</sub> or CF<sub>2</sub>H complexes shown as the starting materials (A) in Scheme III, reaction with BX<sub>3</sub> resulted not in a simple, isolable CX<sub>2</sub> species but in metallacyclic products containing one or two of the PPh<sub>3</sub> phenyl groups linked to the carbene carbon. The reaction sequence A to F shown down the left side of Scheme III has been deduced by comparing the reaction products from the Ru,<sup>6,82</sup> Os,<sup>123</sup> and Ir<sup>75</sup> substrates, A1, A2, and A4, respectively, with BX<sub>3</sub>. From among these reactions one or more of each species A to F has been isolated and fully characterized except for the intermediate B\*, for which there is no direct evidence, and D, which has been spectroscopically observed only. The derivatives prepared from complexes A to F, shown on the right side

SCHEME III<sup>a</sup>

<sup>a</sup>L = PPh<sub>3</sub>; the asterisk (\*) = the intermediate.

of Scheme III, further support the proposed reaction sequence.

The complex  $IrCl_2(CF_3)(CO)(PPh_3)_2$  (A2) reacts with 2 equiv of  $BCl_3$  to produce the highly moisture-sensitive metallacycle C2.<sup>75</sup> A similar reaction with the osmium complex  $OsCl(CHF_2)(CO)(PPh_3)_2$  (A1) gave the much less reactive osmium analogue C1. Both complexes were fully characterized, and the formulation of the Os complex was confirmed by an X-ray crystal structure analysis.<sup>123</sup> The long C-Cl bond in this structure is consistent with the chemical reactivity of the chloroalkyl function. The Cl moiety can be replaced by OMe on reaction with methanol or hydrolyzed to give the metallacyclic acyl complex, which was also characterized by X-ray crystallography.<sup>123</sup>

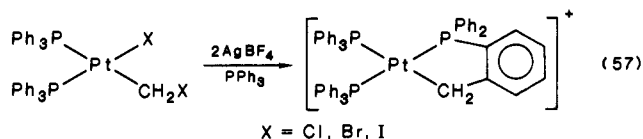
If the reaction time is increased or if excess  $BCl_3$  is used in the reaction with the Ir or Os substrates, then a second cyclization ensues to form the bis-metallacycles E2 and E1, containing bridgehead Cl and H substituents in the Ir and Os complexes, respectively.<sup>75,123</sup> In the reaction of the Ir complex the intermediate cationic chloroalkylcarbene species D2 was characterized spectroscopically, exhibiting a higher  $\nu(CO)$  value than the neutral precursor C2.<sup>75</sup> The Ir and Os bis-metallacyclic complexes E2 and E1 were fully characterized, including a structural determination of the osmium complex. The chemical reactivity of the bridgehead Cl in the iridium complex is evidenced by its reaction with water or ethanol, to form the HO- or EtO-substituted complexes, respectively. The hydroxy complex was structurally characterized.<sup>75</sup> The Cl-, HO-, and EtO-derivatives can be interconverted as shown in Scheme III, probably via the cationic carbene intermediate F.

When  $BBr_3$  is used with the ruthenium complex A4, the cationic bis-metallacyclic product F4 is produced. The bromoalkyl and bromocarbene intermediates B to E are so reactive that no compound containing a C-Br bond is observed, and compound F4 is the first isolable species in the series. This rearranges either in the solid state or on addition of bromide ion to form a neutral bis-metallacyclic carbene complex characterized by X-ray crystallography.<sup>7,74</sup>

The sequence A to F proceeds by  $BX_3$  abstraction of a halide from a haloalkyl species (A, C, E) to form a cationic carbene intermediate (B, D) in which the carbene ligand is sufficiently electrophilic that it attacks the ortho position of an adjacent phenyl ring in a reaction which can be described as intramolecular Lewis acid promoted  $S_EAr$  or an intramolecular Friedel-Crafts reaction. The exception to this sequence is the ruthenium complex  $RuCl(CF_3)(CO)(PPh_3)_2$  which, when treated with  $BCl_3$ , diverges from the scheme at B to form a neutral dichlorocarbene complex.<sup>24</sup>

The relative reactivity of H, Cl, and Br substituents in the metallacycle is evident from comparing the haloalkyl species C and E. Substituents X, Y = Cl, H, as for the osmium complex, result in isolable species which are stable to moisture. The iridium complex has substituents Cl, Cl, and although the products are isolable, they are extremely moisture-sensitive. The Br, Br substituents in the Ru complex are so reactive that neither species is isolable and each rapidly reacts at the C-Br bond.

Intramolecular metallacyclization by an electrophilic methylene species has also been reported and is presumed to proceed via a cationic methylene intermediate (eq 57).<sup>124</sup> An electrophilic carbyne intermediate is implicated in a reaction producing a metallacyclic carbene complex.<sup>125</sup>



#### 4. Comparison of Electrophilic Reactivity

The availability of series of both d<sup>6</sup> and d<sup>8</sup> dihalocarbene complexes,  $L_nM=CX_2$ , and a comparison of the reactions of these species with a wide variety of nucleophiles permit an analysis of the relative electro-

TABLE VI. Qualitative Comparison of Reactivity of Ruthenium Difluorocarbene Complexes ( $L_nRu(=CF_2)$ )

nucleophile	$(PPh_3)_2(CO)_2Ru(=CF_2)$		$(PPh_3)_2(CO)Cl_2Ru(=CF_2)$	
	rate	product	rate	product
H <sub>2</sub> O	slow	$L_nRu(CO)$	fast	$L_nRu(CO)$
ROH	no reaction			$L_nRu(=C(F)OR)$
MeNH <sub>2</sub>	slow	$L_nRu(CNMe)$	fast	$L_nRu(CNMe)$
Me <sub>2</sub> NH	no reaction			$L_nRu(=C(F)NMe_2)$
H <sub>2</sub> NCH <sub>2</sub> CH <sub>2</sub> NH <sub>2</sub>		$L_nRu(CNCH_2CH_2NH_2)$		$L_nRu(=CNHCH_2CH_2NH)$

TABLE VII. Qualitative Comparison of Reactivity of Dihalocarbene Complexes

$L_nM(=CXY)$ (M = Ru, Os)	H <sub>2</sub> O	ROH	HSR
$RuCl_2(=CF_2)(CO)(PPh_3)_2$	fast	fast	no reaction
$OsCl_2(=CFCl)(CO)(PPh_3)_2$	slow	no reaction	$L_nOs(=C(F)SR)$
$MCl_2(=CCl_2)(CO)(PPh_3)_2$	slow	no reaction	$L_nM(=C(SR)_2)$

philicity at the carbene carbon. As expected, the nature of  $L_nM$ , X, and the attacking nucleophile each have a role to play.

First, consider the influence of the metal center. The  $d^6$  complex  $OsCl_2(=CCl_2)(CO)(PPh_3)_2$  requires more severe conditions for hydrolysis than does the ruthenium analogue.<sup>24</sup> Comparing the  $d^8$  Ru and Os complexes, the former reacts slowly with primary amines to form an isocyanide species, but the osmium complex does not react.<sup>76</sup> In both examples the more electron-rich osmium center results in a less electrophilic carbene ligand.

The reactivities of ruthenium  $CF_2$  species in two different oxidation states,  $Ru(=CF_2)(CO)_2(PPh_3)_2$  and  $RuCl_2(=CF_2)(CO)(PPh_3)_2$ , are compared qualitatively in Table VI. The weakly nucleophilic zerovalent complex reacts slowly with water and primary amines but not at all with alcohols or secondary amines, in contrast to the divalent complex which reacts rapidly with all these nucleophiles. The reaction with ethylenediamine results in the strongly electron-withdrawing isocyanide ligand when the substrate is the Ru(0) complex or the much more electron-releasing diaminocarbene ligand with the Ru(II) complex.<sup>23,76</sup> Again, a more electron-rich metal center results in a less electrophilic carbene center.

The effect of the nature of the halide substituent on the reactivity of the carbene is more difficult to assess because the nature of the attacking nucleophile is also important. Table VII presents a qualitative comparison of some reactions of  $d^6$   $L_nRu=CF_2$ ,  $L_nOs=CFCl$ ,  $L_nRu=CCl_2$ , and  $L_nOs=CCl_2$  complexes. The  $CF_2$  complex reacts very fast with water and alcohols and does not react with thiols.<sup>23</sup> The opposite reactivity is observed for the  $CCl_2$  species which react slowly with water and not at all with alcohols but are quite reactive toward thiols.<sup>13,24</sup> In the mixed  $CFCl$  dihalocarbene only the Cl substituent is reactive toward thiols.<sup>77</sup> A simple explanation is found in hard and soft, acid and base theory, where the hard F-substituted carbene is more reactive toward the hard O-based nucleophiles and the softer Cl-containing species prefer the softer S-based reagents. A more rigorous explanation may lie in the proposal that in general reactions of these complexes with the weakly nucleophilic O-based nucleophiles are slow, but in the special case of carbenes with fluorine substituents, F...H...O hydrogen-bonding facilitates the reaction. This enhanced reactivity of fluorocarbene species toward water may explain why  $Fe(TPP)(=CF_2)$  has not been isolated, even though the

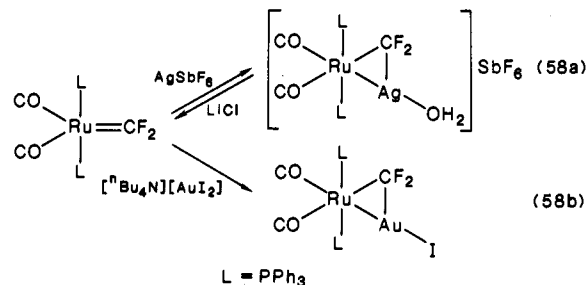
Cl analogue is quite stable.<sup>45</sup>

The charge and ancillary ligands in a difluorocarbene complex also have an important effect on the reactivity. The acetonitrile-substituted cationic derivatives prepared from the  $CCl_2$  and  $CFCl$  complexes discussed in section III.B are all more hydrolytically sensitive than their neutral precursors.<sup>57,77,78</sup> Although the two species  $OsCl_2(=CCl_2)(CO)(PPh_3)_2$  and  $[IrCl_2(=CCl_2)(CO)(PPh_3)_2]^+$  are isoelectronic, the first is a stable isolable species whereas the second has never been observed but is implicated as an intermediate in the electrophilic metallacyclization reactions shown in Scheme III.<sup>13,75</sup> Both these examples illustrate that a higher formal charge renders a complex much more electrophilic. Substitution of a more electron-withdrawing ligand into the coordination sphere has the same effect, as illustrated by the following example. The acetonitrile-substituted osmium cation  $[OsCl(=CCl_2)(CO)(MeCN)(PPh_3)_2]^+$  is an isolable species,<sup>78</sup> but the closely related dicarbonyl cation  $[OsCl(=CHCl)(CO)_2(PPh_3)_2]^+$  is again only suspected to be an intermediate in the sequence shown in Scheme III.<sup>123</sup>

### C. Nucleophilic Reactivity at the Carbene Carbon Atom

Several examples in the previous section demonstrated the much reduced electrophilicity of the zerovalent ruthenium and osmium difluorocarbene complexes. These complexes are unique in dihalocarbene chemistry in that they will also react with electrophiles.

The complex  $Ru(=CF_2)(CO)_2(PPh_3)_2$  forms an adduct with  $AgSbF_6$  to produce the dimetallacyclopropane complex shown in eq 58a. Addition of LiCl reverses



the reaction and precipitates  $AgCl$ .<sup>76</sup> A more stable, neutral adduct is formed when  $[nBu_4][AuI_2]$  is added (eq 58b). In both complexes the value of  $\nu(CF)$  for the adduct is lower than for the  $CF_2$  precursor. The complexes are expected to be isostructural with the AuI adduct of  $OsCl(NO)(=CH_2)(PPh_3)_2$ , which has been characterized by an X-ray crystal structure,<sup>11</sup> and similar to the  $AgCl$  adduct  $OsCl(=C(p-tol)AgCl)(CO)(PPh_3)_2$ , a derivative of the zerovalent osmium *p*-tolylcarbyne complex.<sup>83</sup>

The relationship between reactivity and  $\nu(CF)$  value for  $M=CF_2$  complexes was outlined in section IV, with

TABLE VIII. Ligand Substitution at the Metal Center

substrate	M	X	Y	E	reagent	product	ref
MCl <sub>2</sub> (=CX <sub>2</sub> Y)(CE)(PPh <sub>3</sub> ) <sub>2</sub>					Ag <sup>+</sup> /MeCN	[MCl(=CX <sub>2</sub> Y)(MeCN)(CE)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	
19	Ru	Cl	Cl	O		20	57
21	Os	Cl	Cl	O		22	78
23	Os	Cl	Cl	S		24	57
17	Os	F	Cl	O		18	77
71	Ru	F	NMe <sub>2</sub>	O		74	55
RuCl <sub>2</sub> (=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO)(PPh <sub>3</sub> ) <sub>2</sub> (88)					Ag <sup>+</sup> /CO	[RuCl(=C(Cl)C <sub>4</sub> H <sub>4</sub> N)(CO) <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (89)	82a
IrCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (98)					Ag <sup>+</sup> /MeCN	[IrCl <sub>2</sub> (=C(Cl)NMe <sub>2</sub> )(MeCN)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (99)	57
RuCl <sub>2</sub> (=C(X)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub>							
71		F			CN- <i>p</i> -tol/ClO <sub>4</sub> <sup>-</sup>	[RuCl(=C(F)NMe <sub>2</sub> )(CN- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (73)	24
83		Cl			CN- <i>p</i> -tol/ClO <sub>4</sub> <sup>-</sup>	[RuCl(=C(Cl)NMe <sub>2</sub> )(CN- <i>p</i> -tol)(CO)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup> (85)	23
83		Cl			PMe <sub>2</sub> Ph/ClO <sub>4</sub> <sup>-</sup>	[RuCl(=C(Cl)NMe <sub>2</sub> )(CO)(PMe <sub>2</sub> Ph) <sub>3</sub> ] <sup>+</sup> (86)	57
83		Cl			KSCN	RuCl(SCN)(=C(Cl)NMe <sub>2</sub> )(CO)(PPh <sub>3</sub> ) <sub>2</sub> (84)	57
Cr(=C(Cl)NMe <sub>2</sub> )(CO) <sub>5</sub> (38)					PPh <sub>3</sub> /hν/-10 °C	<i>cis</i> -Cr(=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> )(CO) <sub>4</sub> (41)	82b
[RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(CO)] <sub>2</sub> (97)					PEt <sub>3</sub>	RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> (96)	93
RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (95)					PEt <sub>3</sub>	RhCl <sub>3</sub> (=C(Cl)NMe <sub>2</sub> )(PEt <sub>3</sub> ) <sub>2</sub> (96)	93

low  $\nu(\text{CF})$  values being associated with nucleophilic reactivity. The osmium and iridium d<sup>8</sup> CF<sub>2</sub> complexes, which exhibit higher  $\nu(\text{CF})$  stretches than does Ru(=CF<sub>2</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, form less stable Ag and Au adducts.<sup>37,55</sup> The formation of adducts with electron-deficient metal centers by low-valent, nucleophilic group 8 dihalocarbene, alkylidene, and carbyne complexes can be compared to the complexation of olefinic double bonds to low-valent metal centers and to the coordination of M=C and M≡C bonds to low-valent metals as studied extensively by Stone and co-workers.<sup>126</sup>

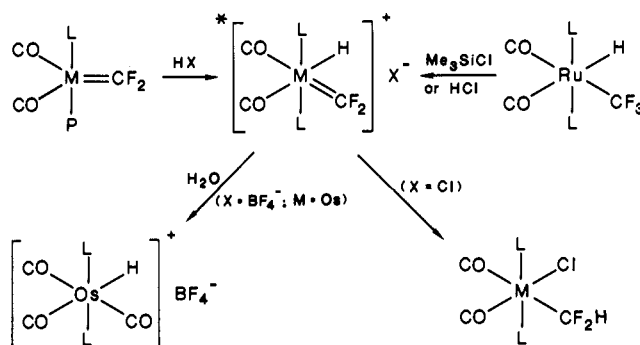
The second important example of nucleophilic reactivity at the carbene carbon atom is the reaction of both ruthenium and osmium dicarbonyl difluorocarbene complexes with H<sup>+</sup>, forming CF<sub>2</sub>H complexes as shown in Scheme IV.<sup>55,76</sup> If nucleophilic reactivity of a carbene complex is charge-controlled, then there are two possible sites of H<sup>+</sup> attack: the electron-rich metal center or the negatively charged carbene carbon atom. Although direct attack of H<sup>+</sup> at the CF<sub>2</sub> ligand to give a coordinatively unsaturated cationic d<sup>6</sup> CF<sub>2</sub>H intermediate can be envisaged, the path shown in Scheme IV is the result of initial H<sup>+</sup> attack at the metal, followed by intramolecular migration to the difluorocarbene ligand in the cationic intermediate. Good evidence for this route is that the same Ru-CF<sub>2</sub>H complex is produced by fluoride abstraction from the *cis*-(trifluoromethyl)hydridoruthenium complex shown in Scheme IV, a reaction in which migration must be taking place.<sup>55</sup> Migration of a hydride to a multiply bonded ligand is a well-known phenomenon, but this is the only example involving a dihalocarbene ligand.

The cationic intermediate shown in Scheme IV is very electrophilic and its susceptibility to hydrolysis of the carbene to a carbonyl ligand is demonstrated by the use of an acid with a poorly coordinating anion, in this case BF<sub>4</sub><sup>-</sup>. The use of HCl results in capture of chloride by the cationic intermediate formed after hydride migration, leading to an isolable difluoromethyl product.

The transformation of a CF<sub>3</sub> to a CF<sub>2</sub>H ligand by fluoride abstraction followed by migration of hydride in a cationic difluorocarbene intermediate has also been observed for the rhodium substrate RhHCl(CF<sub>3</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub>.<sup>52</sup> This reaction was discussed in section III.A and is illustrated in eq 14.

## D. Substitution at the Metal Center

Substitution of a ligand in the coordination sphere other than the carbene ligand was discussed in section

SCHEME IV<sup>a</sup>

<sup>a</sup>L = PPh<sub>3</sub>; M = Ru, Os; the asterisk (\*) = the intermediate.

III.B as a route to new halocarbene complexes. These reactions are collected in Table VIII and will be discussed briefly here.

When an anionic ligand is substituted by a neutral ligand, the product will be a cationic complex. The use of Ag<sup>+</sup> to abstract a labile chloride from a carbene complex, with concomitant coordination of acetonitrile or CO, is a useful route to several cationic dichlorocarbene and monohalocarbene complexes as shown in Table VIII.<sup>55,57,77,78,82</sup> Structural studies indicate that the chloride trans to the dihalocarbene ligand in the neutral precursor is less tightly bound. The stereochemistry of the cationic products is not known with certainty but is not inconsistent with *trans* substitution. In support of this, treatment with silver ion does not easily abstract a chloride from OsCl<sub>2</sub>(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, demonstrating the requirement for a *trans*-labilizing ligand in the coordination sphere.

The cationic dihalocarbene complexes are more hydrolytically sensitive than their neutral precursors, and this may limit the nature of such species that will be isolable. Cationic difluorocarbene complexes are implicated in hydride migration and hydrolysis reactions (section V.C), and some cationic dichloro- and dibromocarbene species are so electrophilic that intramolecular metallacyclization takes place (section V.B). The good  $\sigma$ -donor properties of the acetonitrile ligand complement the strongly electron-withdrawing nature of the halocarbene ligand, with the result that the tightly bound MeCN ligand cannot be substituted by CO or chloride ion.<sup>57</sup>

In the ruthenium haloaminocarbene complexes L<sub>n</sub>Ru(=C(X)NMe<sub>2</sub>) shown in Table VIII the chloride *trans* to the carbene is sufficiently labile that it can be

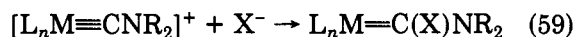


replaced by CN-*p*-tol or PMe<sub>2</sub>Ph without the need for Ag<sup>+</sup>-mediated chloride abstraction. In the latter case the PPh<sub>3</sub> ligands are replaced as well.<sup>23,24,57</sup> Treatment of the chloroaminocarbene complex with KSCN replaces Cl<sup>-</sup> by SCN<sup>-</sup> to give a neutral product.<sup>57</sup>

There are only three examples of simple substitution of a neutral for a neutral ligand. Substitution of PEt<sub>3</sub> for either PPh<sub>3</sub> or CO in the rhodium chloroaminocarbene complexes gives the same product RhCl<sub>3</sub>(=C(Cl)NMe<sub>3</sub>)(PEt<sub>3</sub>)<sub>2</sub>.<sup>93</sup> Photolytic activation of the reaction of Cr(=C(Cl)NMe<sub>2</sub>)(CO)<sub>5</sub> with PPh<sub>3</sub> results in *cis* substitution. This is consistent with a shorter M-CO bond in the *cis* position in pentacarbonyl chromium halocarbene complexes.<sup>98</sup>

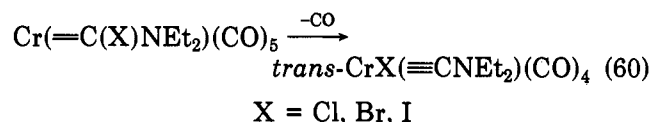
### E. Halide Abstraction and Migration

The utility of cationic aminocarbyne complexes as precursors of haloaminocarbene species, general for all four halides, was described in section III (eq 59).<sup>84-89,122</sup>



In many cases the halide of the carbene ligand is reactive with respect to abstraction or migration to the metal to re-form a carbyne complex. The relative reactivity of the halide substituents gives an insight into the nature of haloaminocarbene complexes.

The species Cr(=C(X)NEt<sub>2</sub>)(CO)<sub>5</sub> (X = F, Cl, Br, I) were all prepared from the cationic pentacarbonyl aminocarbyne precursors by reaction with <sup>n</sup>Bu<sub>4</sub>X at low temperature.<sup>86,87,89</sup> The bromo- and iodocarbene complexes are so reactive that spontaneous rearrangement to the neutral carbyne complex occurs even at low temperature, either in the solid state or in solution. The chlorocarbene requires heating at 30 °C in solution, while the fluorocarbene complex does not react by this route (eq 60). The latter complex decomposes at 100

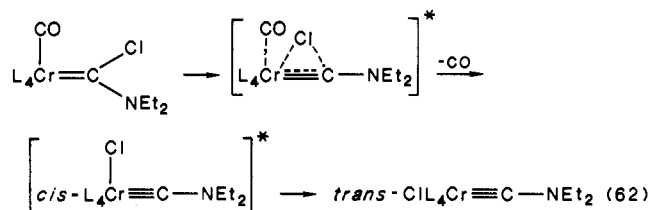


°C but not to the carbyne complex. Thus reactivity follows the order I > Br > Cl > F. In one example a fluoroaminocarbene species can be transformed to a carbyne complex but requires the use of BF<sub>3</sub> to abstract the F substituent (eq 61).<sup>84</sup> A related reaction but one that does not involve halide migration to the metal is the Ag<sup>+</sup> or BCl<sub>3</sub> abstraction of Cl from Cr(=C(Cl)NMe<sub>2</sub>)(CO)<sub>5</sub> to form the cationic carbyne species [Cr(≡CNMe<sub>2</sub>)(CO)<sub>5</sub>]<sup>+</sup>.<sup>82b</sup>



The mechanism of the reaction shown in eq 60 has been investigated and is found to be first order in carbene complex, the rate independent of added CO, PPh<sub>3</sub>, or Cl<sup>-</sup>, and solvent effects to be small.<sup>88,122</sup> The activation enthalpy is independent of C-X bond strength. These factors all indicate that neither CO nor X<sup>-</sup> dissociation is a rate-limiting step. However, the rate is sensitive to the steric bulk of the amino substituent when this factor is varied. These data are all in agreement with a concerted loss of CO and migration of X to the chromium center. Structural studies in-

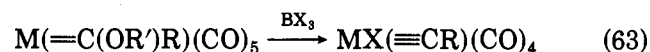
dicating lengthening of the *cis* Cr-CO bond relative to the *trans*.<sup>98</sup> As the *cis* CO ligand dissociates an empty acceptor orbital develops on the metal, oriented toward a lone pair on the carbene Cl substituent, thus the Cl is drawn toward the metal as the CO is lost. The resulting *cis*-substituted carbyne complex then rearranges to the *trans* complex by a previously well-established mechanism (eq 62).<sup>88</sup>



The concerted migration process should be facilitated by increasing the bulk of the alkyl substituent on the amino group, pushing the chloro substituent closer to the metal. Structural studies show that the halide is already bent toward the metal. The CrCX angle is less than 120°, and the CrCN angle is greater than 120° in chromium aminocarbyne complexes Cr(=C(X)NR<sub>2</sub>)(CO)<sub>5</sub> where X is halide, NCO, NCS, Me, SePh, or SnPh<sub>3</sub>.<sup>88,98</sup> Kinetic measurements indicate for X = Cl that R = <sup>i</sup>Pr reacts 10<sup>4</sup> times faster than R = Ph, which in turn reacts 10<sup>3</sup> times faster than R = Me.<sup>88</sup>

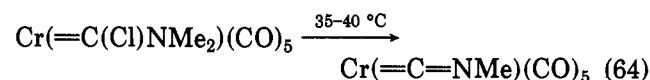
The aminocarbene to aminocarbyne rearrangement is observed for a variety of other migrating groups including SeR, TeR, SnR<sub>3</sub>, and PbR<sub>3</sub>, but not OEt, SiR<sub>3</sub>, NCS, NCO, CN, or F, even though some of the latter contain a large CrCN angle. These substituents do not contain a lone pair in a suitable configuration to participate in the concerted rearrangement described here, which may be the explanation for this phenomenon.<sup>88</sup>

Finally, the use of BX<sub>3</sub> as a reagent for the preparation of group 6 carbyne complexes is a general reaction (eq 63),<sup>127</sup> and the possibility exists that halocarbene

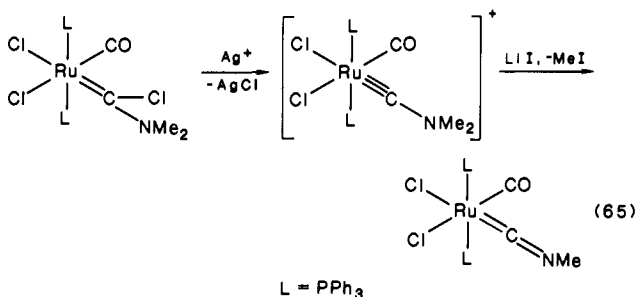


intermediates that rearrange quickly to the corresponding carbyne complex are involved in these reactions. The halocarbene complexes discussed in this review may represent those intermediates which are isolable.

The chloro complex Cr(=C(Cl)NEt<sub>2</sub>)(CO)<sub>5</sub> rearranges to the carbyne complex when heated at 30 °C, but at higher temperature (35-40 °C) an isocyanide complex is formed instead (eq 64). The mechanism is apparently more complex than simple loss of MeCl, and the chlorocarbene is the only complex in the haloaminocarbene series for which this reaction is observed.<sup>89,122</sup>



Halide abstraction from RuCl<sub>2</sub>(=C(Cl)NMe<sub>2</sub>)(CO)(PPh<sub>3</sub>)<sub>2</sub> in the presence of a neutral donor ligand results in the cationic product of substitution at the metal center (section III.D).<sup>24,57</sup> If the complex is treated with Ag<sup>+</sup> in the absence of a neutral ligand, followed by LiI, the elements of MeCl are lost as AgCl and MeI, and the product is the isocyanide complex shown in eq 65.<sup>57</sup> The site of Cl<sup>-</sup> loss is not known, and although an in-



intermediate could be isolated, it proved to be too unstable to characterize. However, spectroscopic evidence supports the cationic aminocarbyne species produced by Cl<sup>-</sup> abstraction from the carbene, as shown in eq 65.<sup>57</sup> This is an intriguing reaction that has implications for the preparation of group 8 carbyne species.

## F. Redox Chemistry

Very little chemistry involving change in the oxidation state at the metal center has been reported for halocarbene complexes. Exceptions are H<sup>+</sup> attack on zerovalent Ru and Os CF<sub>2</sub> complexes (section III.C), Li(*p*-tol)-mediated reduction of the d<sup>6</sup> Os=CCl<sub>2</sub> complex to produce a d<sup>8</sup> carbyne complex (section III.B), and a number of reactions involving the metalloporphyrin halocarbene complexes.

The reductive electrochemistry of Fe(TPP)(CCl<sub>2</sub>) was investigated.<sup>128</sup> Initial two-electron reduction produced a species with the same electrochemistry as the  $\mu$ -carbido dimer Fe(TPP)=C=Fe(TPP), indicating that this complex was the result of attack of a highly reduced species on another molecule.

The carbene ligand did not survive in several oxidation processes involving the same iron dichlorocarbene complex. Air oxidation of Fe(TPP)(=CCl<sub>2</sub>) or Fe(TPP)(=CClR) (R = alkyl) produced Fe(TPP)Cl or [Fe(TPP)]<sub>2</sub>O, and for the former the carbene ligand was lost as O=CCl<sub>2</sub>. The air sensitivity of the halocarbene iron porphyrin complexes is dependent on the nature of both carbene substituents. Halogen oxidation also produces Fe(TPP)X, and when X = Br, Br<sub>2</sub>CCl<sub>2</sub> could be identified. Finally, upon thermal decomposition of Fe(TPP)(=CCl<sub>2</sub>) at over 200 °C the ligand is lost as Cl<sub>2</sub>C=CCl<sub>2</sub>, implicating a bimolecular process.<sup>10,45,79,94</sup>

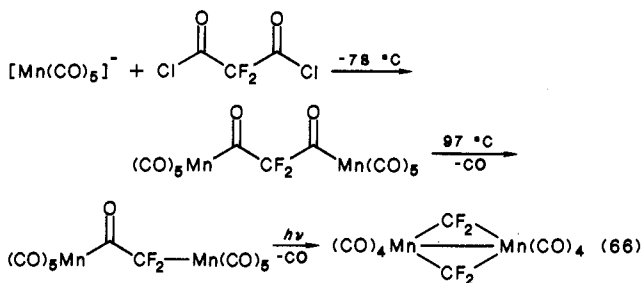
## VI. Halocarbyne and Bridging Halocarbene Complexes

The bonding model for transition-metal dihalocarbene complexes, based on the singlet or triplet ground state of the free carbene fragment, rationalizes why few examples of bridging dihalocarbene complexes are known (section II). In contrast a wide range of bridging methylene and alkylidene complexes display a very rich chemistry.<sup>5,8</sup> The few bridging dihalocarbene and monohalocarbene species that have been reported all involve F as the halide element. All the examples of these species reported to date, and the halocarbyne complexes, are tabulated in Table X, together with relevant IR and NMR data.

### A. Homobimetallic Complexes

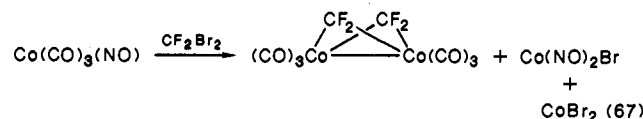
Decarbonylation of trifluoroacetyl species was established as a route to metal CF<sub>3</sub> complexes in section

III.A. In a related reaction, a diacyl halide complex is a precursor to bridging CF<sub>2</sub> species. In the preparation of the manganese complex shown in eq 66 the first



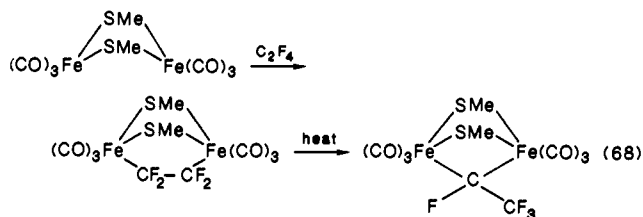
decarbonylation step is thermal but the second requires photochemical activation.<sup>129</sup> The cobalt species  $(\mu\text{-CO})(\mu\text{-CF}_2)[\text{Co}(\text{CO})_3]_2$  is produced by using the same reagent with [Co(CO)<sub>4</sub>]<sup>-</sup>, and subsequent substitution of CO by CNCF<sub>3</sub> yields the derivative  $(\mu\text{-CNCF}_3)(\mu\text{-CO})[\text{Co}(\text{CO})_3]_2$ .<sup>129</sup>

The low-temperature reaction of Na[Co(CO)<sub>4</sub>] with ClCF<sub>2</sub>COCl produces the chlorodifluoromethyl complex Co(CClF<sub>2</sub>)(CO)<sub>4</sub>, which decomposes at room temperature to yield the same  $(\mu\text{-CO})(\mu\text{-CF}_2)[\text{Co}(\text{CO})_3]_2$  species described above, as well as two further CF<sub>2</sub>-bridged complexes,  $(\mu\text{-CF}_2)(\mu\text{-CFCF}_3)[\text{Co}(\text{CO})_3]_2$  and  $(\mu\text{-CF}_2)_2[\text{Co}(\text{CO})_3]_2$ .<sup>59</sup> An alternate synthesis of the latter complex is the photolytic reaction of Co(CO)<sub>3</sub>(NO) with CF<sub>2</sub>Br<sub>2</sub> (eq 67).<sup>130</sup> Similarly, irradiation of CF<sub>2</sub>Br<sub>2</sub> and



Fe(CO)<sub>5</sub> results in the complex  $(\mu\text{-CF}_2)_2(\mu\text{-CO})[\text{Fe}(\text{CO})_3]_2$ . These complexes can be considered to be CF<sub>2</sub>-substituted analogues of Co<sub>2</sub>(CO)<sub>8</sub> and Fe<sub>2</sub>(CO)<sub>9</sub> and follow the same order of stability with the iron dimer more stable than the cobalt dimer.<sup>130</sup>

Thermal rearrangement of a bridging tetrafluoroethylene complex with concomitant CO loss produces a dinuclear iron species containing a bridging CF(CF<sub>3</sub>) ligand (eq 68).<sup>131</sup> NMR data indicate that two species



are present in solution corresponding to syn and anti conformations of the bridging SMe groups, although the X-ray crystal structure of the complex is of the anti conformer. A derivative was produced by exchange of PMe<sub>3</sub> for two terminal CO ligands.<sup>131</sup>

The preference for a bridging alkylidene rather than a bridging fluorocarbene ligand is illustrated by the reaction of [Pt(1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>] with CF<sub>2</sub>=CHF. The product was identified by <sup>19</sup>F NMR and is believed to contain two platinum centers bridged by two  $\mu\text{-C}(\text{H})\text{CF}_3$  ligands, formed by rearrangement of the trifluoroethylene fragment.<sup>132</sup> The rearrangement has proceeded so that the bridging ligand is an alkylidene,

TABLE IX. Structural Data for Bridging Halocarbene Complexes<sup>a,b</sup>

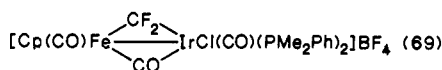
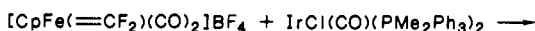
	( $\mu$ -CF <sub>2</sub> ) <sub>2</sub> [Mn(CO) <sub>4</sub> ] <sub>2</sub> (103) Mn, Mn, F, CO <sup>d</sup>	( $\mu$ -SMe) <sub>2</sub> ( $\mu$ -C(F)CF <sub>3</sub> )[Fe(CO) <sub>3</sub> ] <sub>2</sub> (109) Fe, Fe, CF <sub>3</sub> , CO <sup>d</sup>	[Cp(CO)Fe( $\mu$ -CF <sub>2</sub> )( $\mu$ -CO)IrCl(CO)(PMe <sub>2</sub> Ph) <sub>2</sub> ] <sub>2</sub> BF <sub>4</sub> (111) Fe, Ir, F, PMe <sub>2</sub> Ph <sup>d</sup>
M-M'	2.664 (3)	2.963 (6)	2.718 (1)
M-CFX	2.026 (4)	1.848 (5)	1.986 (5)
Ir-CF <sub>2</sub>			2.064 (5)
C-F	c	1.440 (5)	1.37 (1)
FCX	107.2 (2)	100.3 (4)	103.0
M'-L(cis)	1.880 (6)	1.790 (7)	2.335 (1)
M'-L(trans)	1.846 (4)	1.848 (5)	2.423 (2)
Fe-( $\mu$ -CO)			1.807 (6)
Ir-( $\mu$ -CO)			2.392 (5)
ref	129	131	121

<sup>a</sup> Bond lengths in angstroms; bond angles in degrees. <sup>b</sup> Average values for some bond lengths. <sup>c</sup> Data not reported. <sup>d</sup> M, M', X, L.

rather than the alternative fluorocarbene bridge,  $\mu$ -C(F)CHF<sub>2</sub>.

## B. Heterobimetallic Complexes

The electrophilic reactivity of a terminal difluorocarbene complex toward an electron-rich metal center has been exploited in the synthesis of a complex containing Fe and Ir bridged by a CF<sub>2</sub> ligand (eq 69).<sup>121</sup>



The reaction can be formally considered to be oxidative addition of one Fe—C bond of the Fe=CF<sub>2</sub> moiety to the Ir(I) center, thus forming a cationic Ir(III) product. The reaction was unsuccessful for the CCl<sub>2</sub> or CBr<sub>2</sub> iron complexes, reflecting the expected lower stability of bridging CCl<sub>2</sub> or CBr<sub>2</sub> species toward cleavage of the C—X bond. The dinuclear Fe—Ir complex is both thermally and moisture sensitive, demonstrating that the CF<sub>2</sub> ligand is still electrophilic. The dimer is cleaved upon hydrolysis, producing [CpFe(CO)<sub>3</sub>]<sup>+</sup> and IrCl(CO)(PMe<sub>2</sub>Ph)<sub>2</sub> fragments.<sup>121</sup>

In contrast to the previous example, the nucleophilic reactivity of a low-valent Ru complex can lead to the CF<sub>2</sub>-bridged species  $\overline{\text{Ru}}(\text{CF}_2\text{AuI})(\text{CO})_2(\text{PPh}_3)_2$ . Addition of AgSbF<sub>6</sub> to the same Ru precursor produces a related Ag adduct,  $[\overline{\text{Ru}}(\text{CF}_2\text{Ag}(\text{OH}_2))(\text{CO})_2(\text{PPh}_3)_2]\text{SbF}_6$ .<sup>76</sup>

These complexes can be compared to an AuI adduct of the Os methylene complex OsCl(CO)(=CH<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub> and an AgCl adduct of the carbyne complex OsCl(≡C-p-tol)(PPh<sub>3</sub>)<sub>2</sub>, both of which have been structurally characterized.<sup>11,133</sup> The greater stability of these latter species compared to the CF<sub>2</sub>-bridged complexes is further support for the bonding model outlined in section II. The CF<sub>2</sub> bridge-forming reactions can also be considered to be examples of the metalation of M=C double bonds as demonstrated by Stone and co-workers.<sup>126</sup>

## C. Structural Results

Three complexes, ( $\mu$ -CF<sub>2</sub>)<sub>2</sub>[Mn(CO)<sub>4</sub>]<sub>2</sub> (103),<sup>129</sup> ( $\mu$ -SMe)<sub>2</sub>( $\mu$ -C(F)CF<sub>3</sub>)[Fe(CO)<sub>3</sub>]<sub>2</sub> (109),<sup>131</sup> and the  $\mu$ -CF<sub>2</sub>-Fe—Ir-bridged species 111<sup>121</sup> were characterized by X-ray crystallography and show a number of features in common. The structural data are shown in Table IX. Complexes 103, 109, and 111 contain Mn, Fe, and Ir,

respectively, in octahedral geometry, with the shortest M—CF<sub>2</sub> bond (1.848 Å) in complex 109. In 103 the M—CO bond trans to the bridging CF<sub>2</sub> ligand is significantly shorter than that in the cis position. In 109 and 111 the opposite is true, with a longer M—L bond trans to the carbene. The Ir—P distance for the trans phosphine in complex 111 is the longest such bond reported. The FCF or FC(CF<sub>3</sub>) angles are all less than the C sp<sup>3</sup> angle of 108°, although this may not be significant as a big variation is observed in the angle at the carbon in other bridging carbene complexes.<sup>5,8</sup> In complex 111 the CF<sub>2</sub> ligand is symmetrically bridging, but the CO ligand is semibridging with short Fe—C and long Ir—C bonds.

For bimolecular d<sup>7</sup>-d<sup>7</sup> systems with the formula M<sub>2</sub>L<sub>10</sub>, theoretical calculations predict that the bridging form M<sub>2</sub>L<sub>8</sub>( $\mu$ -L')<sub>2</sub> will be favored when L' is a good  $\pi$  acceptor.<sup>134</sup> The three structures can all be considered to be formally d<sup>7</sup>-d<sup>7</sup> systems if CF<sub>2</sub> is counted as a neutral ligand. The manganese  $\mu$ -CF<sub>2</sub> complex 103 can be compared to Mn<sub>2</sub>(CO)<sub>10</sub> which contains no bridging ligands, indicating that bridging CF<sub>2</sub> is a better  $\pi$  acceptor than bridging CO. Similarly, in the Fe—Ir complex 111, replacement of CF<sub>2</sub> by CO is effectively the hydrolysis reaction, which causes dissociation of the dimer showing that a strong acceptor ligand in the bridging position is essential for the integrity of the dimer.<sup>121</sup> The  $\mu$ -methylene ligand is both a better  $\sigma$  donor and  $\pi$  acceptor than the  $\mu$ -CO ligand,<sup>5,8</sup> and replacement of H by F would be expected to improve the acceptor properties.

## D. Spectroscopic Results

Relevant IR and spectroscopic data are shown in Table X. The values of  $\nu$ (CF) and  $\nu$ (CO) for the Ag and Au adducts of the ruthenium CF<sub>2</sub> complex can be compared to  $\nu$ (CF) (1083, 980 cm<sup>-1</sup>) and  $\nu$ (CO) (1983, 1910 cm<sup>-1</sup>) for the zerovalent precursor Ru(=CF<sub>2</sub>)(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>76</sup> The value of  $\nu$ (CF) is almost unchanged upon adduct formation, but  $\nu$ (CO) is increased, reflecting the fact that the acceptor orbitals of the CF<sub>2</sub> fragment are no longer interacting with the ruthenium center alone. The opposite is true for the Fe—Ir dimer which has  $\nu$ (CO) lower than the values of 2115 and 2071 cm<sup>-1</sup> for [CpFe(=CF<sub>2</sub>)(CO)<sub>2</sub>]<sub>2</sub>BF<sub>4</sub>.<sup>31</sup>

The <sup>13</sup>C resonance of the carbene carbon atom in the bridged complexes is found close to 200 ppm. A wide range of values is observed for the <sup>19</sup>F chemical shifts, but when carbene-bound F and CF<sub>3</sub> are in the same molecule as in complexes 109 and 110, then the former

TABLE X. IR and NMR Data for Halocarbyne and Bridging Halocarbene Complexes

	$\nu(\text{CF}), \text{cm}^{-1}$	$\nu(\text{CO}), \text{cm}^{-1}$	$^{19}\text{F}$ NMR, <sup>a</sup> ppm	$^{13}\text{C}$ NMR, <sup>b</sup> ppm	ref
$(\mu\text{-CF}_2)_2[\text{Mn}(\text{CO})_4]_2$ (103)			71.6 <sup>c</sup>		129
$(\mu\text{-CF}_2)(\mu\text{-CO})[\text{Co}(\text{CO})_3]_2$ (104)			44.7 <sup>d</sup>	194.1 <sup>d</sup>	129
$(\mu\text{-CF}_2)(\mu\text{-CNCF}_3)[\text{Co}(\text{CO})_3]_2$ (105)			CF <sub>2</sub> 43.3, 26.1 <sup>c</sup> CF <sub>3</sub> -58.8 $^2J_{\text{FF}} = 12.2$ Hz	$^1J_{\text{CF}} = 390$ Hz 192.3 <sup>d</sup> $^1J_{\text{CF}} = 395$ Hz	129
$(\mu\text{-CF}_2)_2[\text{Co}(\text{CO})_3]_2$ (106)					59, 130
$(\mu\text{-CF}_2)(\mu\text{-C}(\text{F})\text{CF}_3)[\text{Co}(\text{CO})_3]_2$ (107)					59
$(\mu\text{-CF}_2)_2(\mu\text{-CO})[\text{Fe}(\text{CO})_3]_2$ (108)					130
$(\mu\text{-SMe})_2(\mu\text{-C}(\text{F})\text{CF}_3)[\text{Fe}(\text{CO})_3]_2$ (109)			CF 136.8 <sup>d</sup> CF <sub>3</sub> 68.8 $^3J_{\text{FF}} = 7$ Hz CF 130 <sup>d</sup>		131
$(\mu\text{-SMe})_2(\mu\text{-C}(\text{F})\text{CF}_3)[\text{Fe}(\text{CO})_2(\text{PPh}_3)]_2$ (110)			CF <sub>3</sub> 66.6 46.2, 32.4 <sup>d</sup> $^2J_{\text{FF}} = 58$ Hz	202.1 <sup>d</sup>	121
$[\text{Cp}(\text{CO})\text{Fe}(\mu\text{-CF}_2)(\mu\text{-CO})\text{IrCl}(\text{CO})(\text{PMe}_2\text{Ph})_2]\text{BF}_4$ (111)		2045, 1999, 1897			121
$\text{Ru}(\text{CF}_2\text{AuI})(\text{CO})_2(\text{PPh}_3)_2$ (112)	1057, 1000, 978	2029, 1985			76
$[\text{Ru}(\text{CF}_2\text{Ag}(\text{OH}_2))(\text{CO})_2(\text{PPh}_3)_2]\text{SbF}_6$ (113)	1094, 1019	2018, 1943			76
$\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{L}^f$ (114)		2005, 1921		208.7 <sup>e</sup>	135
$\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{L}^g$ (115)					135
$\text{W}(\equiv\text{CCl})(\text{CO})_2\text{L}^f$ (116)					135
$\text{ClC}[\text{Co}(\text{CO})_3]_3$ (117)					137
$\text{FC}[\text{Co}(\text{CO})_3]_3$ (118)			-44.5		43

<sup>a</sup>Chemical shift relative to external  $\text{CFCl}_3$ . <sup>b</sup>Data reported for carbene (or carbyne) carbon atom. <sup>c</sup>Pentane. <sup>d</sup> $\text{CD}_2\text{Cl}_2$ . <sup>e</sup> $\text{CDCl}_3$ . <sup>f</sup>L = hydridotris(3,5-dimethyl-1-pyrazolyl)borate. <sup>g</sup>L = tetrakis(1-pyrazolyl)borate.

is shifted downfield of the latter.

## E. Halocarbyne Complexes

The scope of halocarbyne species is extremely limited, with a single example of a terminal and two of triply bridging CX species.

When  $\text{CH}_2\text{Cl}_2$  was used as the solvent in a study of free radical oxidation of  $[\text{Mo}(\text{CO})_3\text{L}]^-$  by  $[\text{Me}_2\text{NC}_6\text{H}_4\text{N}_2]^+$ , the fortuitous product was the chlorocarbyne complex  $\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{L}$  (L = hydridotris(3,5-dimethyl-1-pyrazolyl)borate). The tungsten analogue was also prepared, and the molybdenum species with L = tetrakis(1-pyrazolyl)borate was characterized structurally.<sup>135</sup> The reaction was proposed to proceed via production of the radical species  $^{\bullet}\text{CHCl}_2$  from the solvent, which then attacked the metal center to form, in sequence,  $-\text{CHCl}_2$ ,  $=\text{CHCl}$ , and  $\equiv\text{CCl}$  complexes. The crystal structure shows short  $\text{Mo}\equiv\text{C}$  and  $\text{C}-\text{Cl}$  bond lengths of 1.89 (1) and 1.55 (1) Å, respectively.

The reaction of the electrophilic carbyne center in  $\text{Mo}(\equiv\text{CCl})(\text{CO})_2\text{L}$  with  $\text{ER}^-$  (ER = SMe, SPh, SePh, Se-*p*- $\text{C}_6\text{H}_4\text{NO}_2$ ) or PhLi results in substitution of the Cl ligand to form new  $\text{Mo}=\text{CER}$  or  $\text{Mo}\equiv\text{CPh}$  carbyne species, and reaction with  $\text{Li}_2\text{E}$  (E = S, Se, Te) produces the anionic chalcocarbonyl complexes  $[\text{Mo}(\text{CE})(\text{CO})_2\text{L}]^-$ .<sup>136</sup>

Dicobalt octacarbonyl reacts with  $\text{HgPh}(\text{CCl}_3)$  or  $\text{CCl}_4$  to produce the cluster complex  $\text{ClC}[\text{Co}(\text{CO})_3]_3$ .<sup>137</sup> Both precursors have been shown to be sources of free  $:\text{CCl}_2$ , by trapping with cyclohexene to form norcaradiene.<sup>56</sup> A bridging dichlorocarbene complex, the chloro analogue of  $(\mu\text{-CO})(\mu\text{-CF}_2)[\text{Co}(\text{CO})_3]_2$ ,<sup>129</sup> was proposed to be an intermediate in the formation of the chlorocarbyne cluster complex, although the variety of reaction products observed implies a radical mechanism.<sup>137</sup> Either thermal or photolytic activation of the reaction of  $\text{Co}_2(\text{CO})_8$  with  $\text{CF}_3\text{I}$  produces the fluorine-substituted analogue  $\text{FC}[\text{Co}(\text{CO})_3]_3$ .<sup>43</sup>

## VII. Conclusions

The decade since the first transition-metal dihalocarbene complex was reported has seen steady progress in the area. In one sense the diversity of metal carbene reactivity is represented, with examples of both nucleophilic and electrophilic dihalocarbene complexes. However, two limitations are evident from this review. The reactivity of halocarbene complexes does not so far extend to the carbene transfer reactions like olefin metathesis or cyclopropanation. Secondly, the dihalocarbene complexes reported to date are largely represented by Group 8 species with strong metal-carbene bonds. These two observations may be related by a common explanation. Carbene transfer type reactivity might be expected for halocarbene complexes from groups 6 and 7 and earlier. However these species either are too reactive to be isolated or are presently unknown. The singlet ground state of the free halocarbene fragment may render the formation and stability of early-transition-metal dihalocarbene complexes energetically unfavorable. From a practical standpoint, new dihalocarbene-transfer reactions would not be particularly useful to organic chemists who already have a good arsenal of dihalocarbene sources.<sup>56,138</sup>

The synthesis of dihalocarbene complexes has taxed the ingenuity of synthetic organometallic chemists, yet the result is still that each class of complexes is prepared by a unique route that is not generally applicable. There is still room for chemical creativity in approaching potential new complexes. The conclusions drawn from the discussions of structural and spectroscopic properties highlight the need for a more systematic approach to gathering data from which good comparisons of isostructural species may be made. The limited amount of NMR spectroscopic data available is disappointing, and this situation must be rectified.

The real utility of dihalocarbene complexes to data is in ligand modification. Organometallic chemists may look to this chemistry as a means of first creating a

metal-carbon bond and then subsequently building on the remainder of a ligand by exploiting the rich nucleophilic substitution chemistry of dihalocarbene complexes. The potential of coordinated dihalocarbenes as precursors to novel carbyne species has been largely unexplored.

Finally, there is one other arena where dihalocarbene complexes may be significant. There is evidence that metal-bound dihalocarbene species may be formed during the reductive metabolism of polyhalogenated substrates at the iron heme active site of cytochrome P<sub>450</sub><sup>139</sup>. The iron porphyrin halocarbene complexes discussed here may be good models for these intermediates.

### VIII. Acknowledgment

We wish to thank Dr. E. A. Carter and Professor D. F. Shriver for providing unpublished material. P.J.B. is grateful to the New Zealand University Grants Committee for the award of a postdoctoral fellowship.

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