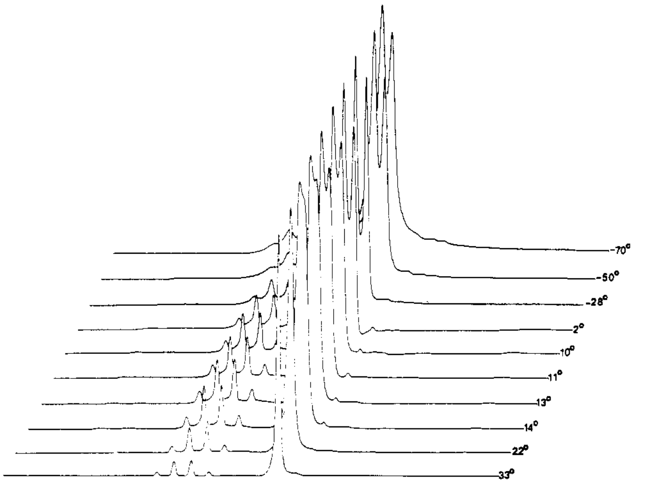

Figure 3. Variable-temperature ^1H NMR spectra of $C_5H_5FeC_5H_3(CHMeNMe_2)(SCSNMe_2)$ (4).

NMR parameters, rate constants, and an approximate value of the barrier to rotation in compounds **1**, **2**, **4**, and **5** are given in Table III. The rate constant, k_c, at the coalescence temperature, T_c, was determined from the peak separation, $\Delta\nu$, at slow exchange by using the equation $k_c = \pi\Delta\nu/(2)^{1/2}$ or $k_c = \pi[\Delta\nu^2 + 6J^2]^{1/2}/(2)^{1/2}$ for coupled systems.[15] An approximate rotational free energy barrier was obtained from the Eyring equation: $\Delta G^\ddagger = 2.3RT[10.3 - \log(k_c/T_c)]$. The values of the rotational barriers are 15.8 ± 0.3, 16.2 ± 0.3, 15.4 ± 0.3, and 15.8 ± 0.3 kcal/mol, for **1**, **2**, **4**, and **5**, respectively. The rotational barrier of $SCSNEt_2$ in **2** and **5** is higher than that of $SCSNMe_2$ in **1** and **4** because the diethylamino group has higher steric hindrance than the dimethylamino group in a 1,2-disubstituted cyclopentadienyl ring.

Hollaway[16] has determined rotational barriers about the carbamate C–N bond in a series of *N*,*N*-dialkyldithiocarbamate esters. Activation energies of 10–12 kcal/mol suggested that an appreciable amount of C–N double-bond character was present. Hollaway was able to correlate the C–N double-bond character with the "thioureide" band between 1489 and 1498 cm^{-1} in the infrared region. The "thioureide" band that has been assigned to the partial double-bond character in carbon–nitrogen bond was observed at 1498 and 1487 cm^{-1} for the dimethyldithiocarbamate derivative **1** and the diethyldithiocarbamate derivative **2**, respectively, and at 1495 and 1498 cm^{-1} for derivatives **4** and **5**, respectively.

The variable-temperature ^1H NMR spectra for the dialkyldithiocarbamate derivatives **1**, **2**, and **4** are shown in Figures 1, 2, and 3, respectively. At low temperature, the ^1H NMR spectrum consists of two singlets for two methyl groups of **1** and of two triplets and two quartets for two methyl and two methylene groups of **2**. As the temperature is raised, the signals broaden, and at fast rotation all of the signals become singlets.

The infrared region, between 970 and 1010 cm^{-1}, is associated with the $\bar{\nu}$(CSS) vibrations and has been used to differentiate between monodentate and bidentate dithiocarbamate ligands. The compounds $C_5H_5Fe(C_5H_3\text{-}1\text{-}CH_2NMe_2\text{-}2\text{-}SCSNR_2)$ (R = Me, Et) exhibit two bands at 972, 998 and 978, 1003 cm^{-1}, respectively. On the basis of work by Bonati and Ugo,[17] the strong band at 972 and 978 cm^{-1} can be assigned to an uncomplexed C=S stretch. Caution must be observed as absorption from the ferrocene moiety is found in this region around 1000 cm^{-1}. Many studies have supported the use of the bands in 950–1050 cm^{-1} region to ascertain whether the dithiocarbamate ligand is monodentate or bidentate.[18]

Registry No. 1, 112532-16-8; 2, 112532-18-0; (*R*)-3, 31886-58-5; 4, 112532-17-9; 5, 112532-19-1; [(dimethylamino)methyl]ferrocene, 1271-86-9; tetramethylthiuram disulfide, 137-26-8; tetraethylthiuram disulfide, 97-77-8.

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Theoretical Study of the Conformation of *cis*-Bis(carbene) Complexes

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Received April 27, 1987

The conformation of transition-metal *cis*-bis(carbene) complexes has been studied by means of extended Hückel calculations. To understand the preferred conformations of the complexes, back-donation and the interaction between a σ M–L (L = CR_2) bond and an empty p_C orbital situated on the adjacent cis carbene group, which will be referred to as an M–L/ligand interaction, must be considered. Back-donation favors the edge-to-edge (E,E) conformation while the M–L/ligand interaction favors the face-to-face (F,F) conformation. The relative importance of the two effects depends on the nature of the metal, ancillary ligands, and substituents on the carbenes. In the complexes with high-lying d orbitals and no deactivated carbenes, the back-donation predominates while in the complexes with low-lying d orbitals and deactivated carbenes, the M–L/ligand interaction is dominant. The conformation of single faced π-acceptor ligands such as carbene and olefin (see also ref 8a of this work) can thus be fully analyzed with these two factors.

Transition-metal carbene complexes are key intermediates in numerous organometallic reactions[1] especially for the transformations of conjugated systems such as olefin metathesis and polymerization and the formation of small

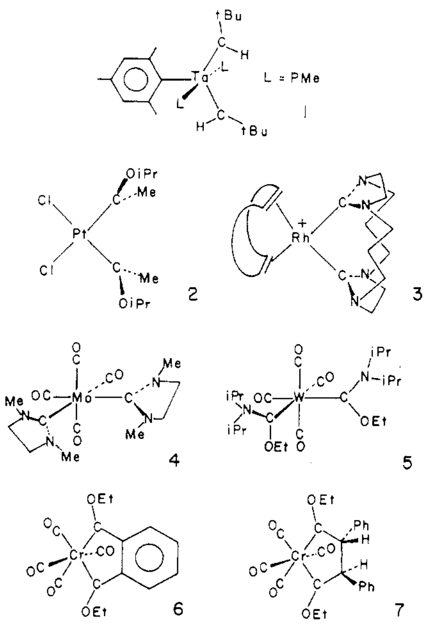
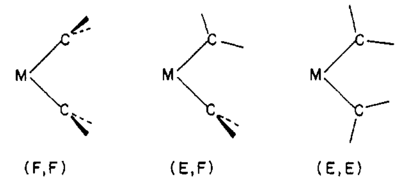


Figure 1. Structurally characterized *cis*-bis(carbene) complexes.

rings. Since the pioneering work of E. O. Fisher,[2] many such complexes with various metal centers have been synthesized and structurally characterized.[3] They form essentially two types of complexes: the Fisher-type complex with M^-–C^+ polarity in which the carbene carries π-electron donor groups and the Schrock-type alkylidene complex with an M^+–C^- polarity. Metals may coordinate more than one carbene which has lead to the synthesis of polycarbene complexes containing up to six carbenes on a single metallic center.[4] Among these polycarbene complexes, *cis*-bis(carbene) complexes are of special interest. In some cases, they seem to result from a dissociative addition of an olefin to a metallic center.[5] The reverse coupling process has not yet been observed for carbenes but has been reported for carbyne and carbon monoxide.[6] Coupling between carbene and carbone monoxide has also been observed.[6] Theoretical studies by Hoffmann et al. of the C–C bond cleavage and bond coupling in monometallic[7a] and bimetallic[7b] systems have shown that the dissociative addition requires the presence of strong π-donating groups on the olefin. Therefore only strongly deactivated olefins can dissociate in agreement with the experimental findings of Lappert.[5]

Chart I



The coupling of carbenes requires a specific orientation. In a least motion pathway the plane of each carbene is perpendicular to the C–M–C coordination plane. Since this orientation may not be the most favorable[7b] or may even be difficult to reach, it is of interest to delineate the factors that favor such a coupling orientation. Although a least motion pathway may not be followed by the system, the potential energy surface of the real coupling reaction should still bear some characteristic of the rotation barrier of the bis(carbene) complex. The knowledge of the energy difference between the conformers is thus of importance for a better understanding of these complexes. The theoretical study of the conformation of carbene–olefin complexes[8a] has shown that the relative orientation of two single faced π-acceptor groups is strongly influenced by the nature of the ancillary ligands. This suggests that the preferred conformation of a bis(carbene) complex may also strongly depend on the ancillary ligands. In this work, we discuss the relative conformations of a *cis*-bis(carbene) complex as a function of the metal, ligand field, ancillary ligand groups, and carbene substituents.

An examination of the available experimental data provides the structurally *cis*-bis(carbene) complexes shown in Figure 1. the d^8 Pt and Pd complexes **2**[9] and **3**[10] contain carbene planes perpendicular to the coordination plane. This face-to-face (F,F) orientation favors the C–C coupling. This (F,F) orientation is not only a result of the saturated $(CH_2)_3$ backbone in **3**, since such a constraint does not exist in **2**, though steric effects in **2** certainly favor such an orientation. In the trigonal-bipyramid (TBP) tantalum complex **1**[11] the two carbenes occupy two of the equatorial sites and lie in the equatorial plane in an edge-to-edge (E,E) orientation. Note that the two carbene groups are agostic[12] since the Ta–C–*t*-Bu angles are respectively 154° and 168.9° instead of the expected 120°. This well-documented structural distortion, initially studied theoretically by Hoffmann[13a] in the tantalum complexes, has attracted considerable attention from other theoreticians.[13b-d] The d^6 octahedral Mo complex **4**[14a] exhibits another orientation

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for the two cis carbenes. The conformation can be described by a 45° conrotatory motion of the two carbene planes away from an (F,F) orientation. The same type of orientation has also been observed for the d^6 tungsten complex **5**.[14b] The structures of the related octahedral d^6 chromium complexes **6**[15] and **7**[15] provide a worthwhile comparison. In **6**, the two carbenes are part of a conjugated chelating ring that forces an (E,E) orientation while the chelating carbenes of **7** are not part of a conjugated system allowing the carbenes to be skewed with dihedral angles between the carbene planes and the coordination plane of 16° and 37°. As a result of this lack of symmetry, the two Cr–C bond lengths in **7** are different (1.98 and 2.02 Å), the shorter of which belongs to the carbene unit with the smaller torsional angle.

This presentation of the experimental data clearly indicates that the carbene complexes can exhibit a large variety of conformations. The following discussion, based on extended Hückel calculations, will suggest reasons for this variation of structures. Our analysis will be limited to the comparison of the three limiting conformations: (E,E), (F,F), and (E,F) in which only one carbene is rotated by 90° with respect to the (F,F) conformation (Chart I). These three conformations provide a sufficient description of the shape of the entire potential surface for the coupled rotation of the two carbenes as previously shown in the study of carbene–olefin complexes.[8a]

Although considerable theoretical work has been devoted to mono(carbene) complexes,[16] little attention has been given to two single π-faced groups bonded to one metal.[7a,14c,17] In the general bonding description of these systems, a carbene is considered to be a neutral ligand, whether it is a Fisher carbene or an alkylidene complex. Each metal–carbon σ-bond originates from the in-phase combination of one empty metal σ-hybrid orbital and the σ-carbene lone-pair orbital (**8**) which does not by itself lead to a conformational preference. The empty carbene p_C orbital may be involved in two types of interaction. One is the well-known d_π/p_π back-donation between an occupied metal nonbonding d orbital and the empty p_C orbital **9**. The other interaction has been described in detail in previous work on metal carbene–olefin complexes.[8a] As schematically shown in **10** an occupied M–L σ bond can be stabilized by an empty p_C orbital situated on a cis carbene group if the M–L σ bond and the carbene p_C orbital are coplanar. This stabilization results from a through-space overlap with the part of the M–L σ bond localized on L since the metal contribution is usually from atomic orbitals of symmetry such that they cannot overlap directly with the p_C orbital. Rotation of the carbene by 90° brings the M–L σ bond into the nodal plane of the p_C orbital and annihilates this stabilization. It is important to be aware that, in a real complex, many M–L σ bonds can compete for the same stabilization since the carbene is cis to more than one L group. In the typical occupied/empty orbital interaction, stabilization of the energetically highest M–L σ bond is preferred. In the present study of *cis*-bis(carbene) complexes, the metal–carbene σ bond is in fact the energetically highest one. This is easily understood by noting that the M–L σ bond, being more centered on L, has an energy related to that of L. Calculations indicate that the σ orbital of CH_2 is energetically higher than that of other ligands like Cl or CO which results in an energetically higher M–carbene σ bond. This interaction between a M–L σ bond and an empty orbital situated on a cis ligand was initially observed in a study of the conformation of carbene–olefin complexes where it was found to play an important role.[8a] For convenience we have called it an *M–L/ligand interaction.*

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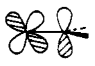

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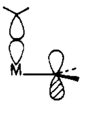

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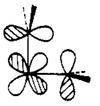
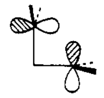
Table I. Sum of the Energies of the Occupied d Orbitals and Total Energy (kcal/mol) Relative to the Best Conformation for $H_3Ta(CH_2)_2^{2-}$

	conformation		
	(E,E)	(E,F)	(F,F)
$\sum d$	0.	30.5	56.4
ΔE_{tot}	0.	25.9	50.6

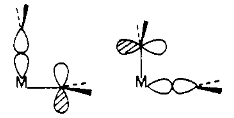
The point to notice is that the two above interactions do not favor the same conformations. *For strictly degenerate d orbitals, the maximum of back-donation is reached when two different d orbitals are stabilized by two p_C orbitals.*[8b] This makes (F,F) highly unfavorable since in this conformation, *one and only one d orbital overlaps with the two p_C carbene orbitals* (in-phase combination of p_C as shown in **11a**). The corresponding out-of-phase combination of the two p_C orbitals (**11b**) does not have the proper symmetry to overlap with any metal d orbital. In contrast, as shown in **12**, the (F,F) orientation allows the two carbene p_C orbitals to be used in a M–L/ligand-type interaction. This may favor (F,F) with respect to (E,E) or (E,F) if the metal–carbene σ bonds are the energetically highest σ bonds of the molecule.



11a



11b



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Although it is difficult to know which interaction dominates in a given complex, since this depends on the nature of the metal, ancillary ligands, and substituents on the carbenes, some general trends can be indicated from the results of ref 8a. Complexes with high-lying and diffuse d orbitals such as early-transition-metal complexes with no or few π-accepting ligands are dominated by the back-donation phenomenon. Late transition metals, accumulation of π-accepting ligands on any type of metal center, and π-donating substituents on the carbene group tend to diminish the role of back-donation and therefore enhance the role of the M–L/ligand interaction. Using this general bonding framework, we will now discuss each complex shown in Figure 1 (see Appendix for details of parameters and geometry).

Tantalum Complex 1

In this early-transition-metal complex, the phenyl ring is not a strong π-accepting ligand and the carbene ligands are not substituted with π-donating groups. Thus $H_3Ta(CH_2)_3^{2-}$ should be a reasonable model for studying compound **1**, and its conformational behavior should be primarily dictated by back-donation.

With the two carbenes occupying the equatorial sites, the (E,E) conformation is calculated to be considerably more stable than (E,F) (26 kcal/mol) or (F,F) (51 kcal/

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[15] Schubert, U.; Ackermann, K.; Hoa Tran Huy, N.; Roll, W. *J. Organomet. Chem.* **1982**, *232*, 155. See also: Hoa Tran Huy, N.; Fisher, E. O.; Riede, J.; Thewalt, U.; Dötz, K. H. *J. Organomet. Chem.* **1984**, *273*, C29.

[16] See ref 16 and 17 in ref 8a.

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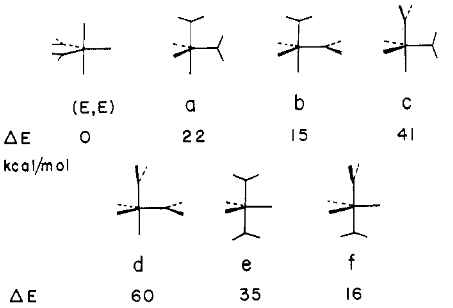
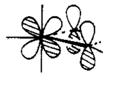
Chart II



mol). The dominant influence of the back-donation accounts well for this ordering since the energy of the occupied d orbitals and the total energy vary in a parallel manner, as shown in Table I.

The basic d orbital splitting for a TBP in absence of any π interaction is well-known.[18] The two orbitals of lowest energy are the nonbonding e'' set, xz and yz. The slightly antibonding e' set, $x^2 - y^2$ and xy, are of higher energy and, considerably higher in energy, is the z^2 orbital. Four electrons, counting the carbene as neutral, have to be housed in the d block. Adding the π effect to the above d splitting is a straightforward matter. In (E,E), xz and yz are stabilized by the in-phase **13** and out-of-phase **14** combination of the two p_C orbitals while the e' set remains unaffected. In contrast, in (E,F), only one orbital of the e'' set, the appropriate combination of xz and yz is stablized by the carbene that still lies in the equatorial plane. The d orbital that can interact with the rotated carbene is a combination of $x^2 - y^2$ and xy and remains intrinsically higher in energy. In (F,F), $x^2 - y^2$ overlaps with the inphase combination of the two carbene p_C orbitals (**15**) and arrives at a lower energy than xz and yz which are destabilized by the filled π_{CH_2} orbital of each carbene. As illustrated by **11b**, no d orbital has the adequate symmetry to be stabilized by the out-of-phase combination of the two p_C orbitals in an (F,F) orientation. It is thus clear that the most stable location for four electrons is in the xz and yz orbitals of the (E,E) conformation.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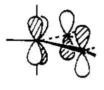
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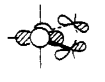
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It is interesting to note that the presence of agostic carbenes does not modify the above conformational order. As it has been shown in previous work,[13a,d] the agostic interaction requires the presence of low-lying empty orbitals on the metal to increase the interaction between the metal and the σ lone pair of the carbene. In an (E,E) conformation $x^2 - y^2$ and xy are empty and thus prepared to play that role.[13a] However, the presence of agostic interactions may reverse the conformational preferences found on the sole basis of the most efficient back-donation. For instance, by rotating one of the carbene group by 90° an orbital of e'' symmetry is left formally empty and can thus interact more efficiently with the carbene σ orbital because it is of lower energy than an e' orbital. However, the amount of stabilization resulting from an agostic interaction is small (15 kcal/mol)[13a,e] relative to the difference in energy between (E,E) and the other conformations. Thus the (E,E) conformation is the most stable even in presence of the agostic interactions.

Table II. Sum of the Energies of the Occupied d Orbitals and Total Energy (kcal/mol) Relative to the Best Conformation for $H_2Rh(CH_2)_2^-$

	conformation		
	(E,E)	(E,F)	(F,F)
$\sum d$	0	7.9	26.8
ΔE_{tot}	2.8	0	4.4

Table III. Sum of the Energies of the Compound d Orbitals and Total Energy (kcal/mol) Relative to the Best Conformation for $(Ethylene)_2Rh(CH_2)_2^+$

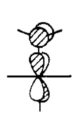
	conformation		
	(E,E)	(E,F)	(F,F)
$\sum d$	23.1	18.0	0.0
ΔE_{tot}	26.6	8.8	0.0

So far, we have only considered isomers in which the two carbenes occupy the equatorial sites of a TPB. Complexes with carbenes in apical positions have been observed for later transition metals,[19] but, to our knowledge, no such structure has been observed with early transition metals. In order to determine if a bis(carbene) with one or two apical carbenes was viable for tantalum d^4 complexes, we performed calculations on all possible isomers and conformers. The results are shown in Chart II. The preferred structure is clearly the (E,E) diequatorial isomer. However, putting one or two carbenes at an apical site, such that back-donation from xz or yz is possible (structures b and f of Chart II), is energetically less demanding than the rotation of one carbene in the diequatorial isomer. For any of the configurations, maximizing the back-donation by allowing overlap between xz or yz with p_C gives the energetically favored rotamer. This proves once more the importance of back-donation in this complex.

Square-Planar ML_4 Complexes 2 and 3

Because the metal centers of complexes **2** and **3** are more electronegative than tantalum, they are less likely to be influenced by back-donation. In addition, the two carbenes are substituted by π-donating ligands that diminish even more the influence of back-donation. The ancillary ligands appear to have no influence on the adopted conformation since **2** carries π-donating ligands (Cl) and **3** carries π-accepting ligands (COD). In order to systematically analyze the factors at work in these complexes, we used $H_2Rh(CH_2)_2^-$ as a model for d^8 $L_2M(CR_2)_2$ and the substituent effects were introduced progressively.

In the coordinate axes with z perpendicular to the molecular plane, the three fully nonbonding orbitals are xz, yz, and xy. The z^2 orbital is slightly higher in energy while $x^2 - y^2$ is out of the bonding picture. In (E,E), both xz and yz overlap with a carbene p_C (**16** and **17**). In (E, F), the



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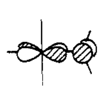
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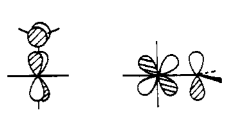

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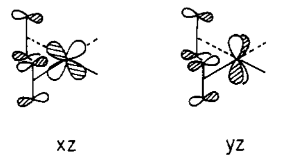
situation is similar with *xz* or *yz* replaced by *xy*, 18. The two conformers thus have similar back-bonding properties in contrast to the (F,F) case where only *xy* has the symmetry to overlap with the two carbene p_C orbitals as shown in **11a**.

From the general bonding description, (E,E) and (E,F) should, to a first approximation, be of equal energy and considerably more stable than (F,F) if back-donation has the dominant influence. Numerical results from the model compound $H_2Rh(CH_2)_2^-$, reported in Table II, do not confirm this trend. The total energy differences indicate very small rotational preferences while the energy of the d block strongly disfavors (F,F). Steric hindrance does not account for this discrepancy between the energy of the d block and the total energy since the distance between the closest H atoms of the two carbenes is greater than 2.2 Å. In this simple model of the real compound, back-donation has no longer the dominant influence. A M–L/ligand interaction must be invoked to interpret the results. Recall that the M–L/ligand stabilization is maximized for an (F,F) orientation. Since the preferred conformation will depend on the relative weight of both effects, a better representation of the real compounds by a progressive introduction of the substituents effects is necessary.

(a) π-Acceptor Ligands. The introduction of COD trans to the two carbenes as in **3** causes a significant modification of the simple bonding scheme obtained for the less substituted compound. The COD, modeled by two ethylenes, is perpendicular to the coordination plane so that the two π^*_{CC} orbitals stabilize *xz* and *yz*, **19**, but leave *xy* unchanged. This results in a reduced back-donation from the *xz* and *yz* orbitals to the carbene p_C orbitals. To achieve maximum stabilization by back-donation, the two p_C orbitals must overlap only with *xy* in an (F,F) orientation rather than with the two deactivated *xz* and *yz* orbitals. (E,E) and (E,F) are thus disfavored relatively to (F,F) as shown from the value of $\sum$d, the energy of the d block, in Table III. It should be noted that this is the first system where we have seen back-donation favor the (F,F) orientation. Addition of the M–L/ligand interaction, earlier seen to favor (F,F), leads to a definite preference for the (F,F) conformation (see Table III). The nondegenerate nature of the nonbonding d block caused by the presence of the π^*_{CC} orbitals from COD has caused π-acceptor groups on the metal to apparently increase the rotational barrier of the two carbenes rather than diminish it, as is usually found.



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π-Donor substituents on the two carbenes clearly diminish the role of the back-donation from the metal but seem to have less influence on the M–L/ligand interaction.[8a] However, since in the complex both factors are working coherently to favor (F,F), no change in the optimal conformation is to be expected. (F,F) is found to be 13.4 kcal/mol lower than (E,F) in $(COD)Rh(C(NH_2)_2)_2^+$, and (E,E) is highly unfavorable for additional steric reasons.

(b) π-Donating Ligands on the Metal. The introduction of two chlorine ligands in **2** equally destabilizes *xz*, *yz*, and *xy*. This complex resembles the nonsubstituted model; however, the metal to carbene back-donation should play a larger role, thus favoring (E,E) over the other conformers. As expected, the energy of the d block shows a stabilization of 19.8 kcal/mol for (E,E) over (F,F) in $Cl_2Pt(CH_2)_2$ as compared to the 13 kcal/mol calculated for $H_2Pt(CH_2)_2$. However, even with Cl ligands bonded to the metal, the back-donation is not the driving force for the conformational preference. The M–L/ligand interaction takes precedent favoring the (F,F) conformation. This is in agreement with the calculated 2.1 kcal/mol stabilization of the (F,F) $Cl_2Pt(CH_2)_2$ over the (E,E) conformer. When compared to the 7 kcal/mol stabilization of the (F,F) conformation in $H_2Pt(CH_2)_2$, it is seen that π-donating ligands significantly diminish the preference for the (F,F) conformation but not enough to reverse the conformational preference. For each of the calculated complexes, the energy of (E,F) is found intermediate between that of (E,E) and (F,F).

Table IV. Extended Hückel Parameters with Double-ζ Expansion (Coefficients in Parentheses) for the d Orbitals

atom	orbital	ζ	H_{ij}
Pt	6s	2.55	−9.08
	6p	2.55	−5.48
	5d	6.01 (0.632 99)	−12.59
		2.70 (0.550 94)	
Ta	6s	1.89	−10.1
	6p	1.85	−6.86
	5d	4.08 (0.657 20)	−12.1
		1.64 (0.566 80)	
Rh	5s	2.135	−8.09
	5p	2.100	−4.57
	4d	4.29 (0.580 70)	−12.5
		1.97 (0.568 50)	
Mo	5s	1.96	−8.34
	5p	1.90	−5.24
	4d	4.54 (0.598 81)	−10.50
		1.80 (0.598 81)	
Cr	4s	1.70	−8.66
	4p	1.70	−5.24
	3d	4.95 (0.487 61)	−11.22
		1.60 (0.720 51)	

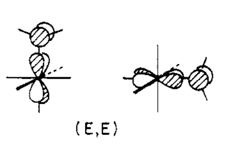
Substituting OH for H on the carbene further diminishes the role of back-donation and increases the role played by the M–L/ligand interaction such that, in $Cl_2Pt(CHOH)_2$, (F,F) remains 1.5 and 5 kcal/mol lower than (E,F) and (E,E), respectively. It should be noted that the electronic control of the rotational barrier is minimal in this complex and that steric constraints favoring the (F,F) conformation may dominate.

In summary for square-planar complexes, the (F,F) conformation is preferred for all type of ligands and carbene substituents. This may be explained by the presence of a late transition metal giving minimal importance to the back-donation and thus allowing the M–L/ligand interaction to dominate. With π-accepting ancillary ligands back-donation and metal–L/ligand interaction work together to favor (F,F), indicating a potentially high rotational barrier for the carbenes. Note finally that a similar (F,F) structure has been found for a tetracarbene d^8 platinum complex.[4]

ML_6 d^6 Octahedral Complexes

As in the nonsubstituted square-planar system, (E,E) and (E,F) should be stabilized by equivalent back-donation, since both conformations allow each p_C orbital to overlap with a different d orbital, **20** and **21**, and (F,F) should be the least favored.

The attachment of four CO groups to the metal, **4**, **6**, and **7**, causes an equal stabilization and delocalization of the three nonbonding orbitals of the t_{2g} set. Accordingly, (E,E) and (E,F) should remain equivalent and both should be preferred over (F,F). However, the π-accepting CO ligands have reduced the influence of back-donation al-



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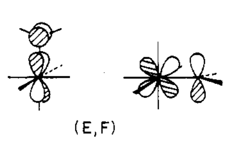

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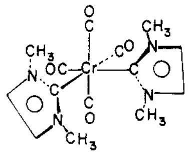
lowing the M–L/ligand interaction, favoring (F,F) to become a competing influence. It is difficult to assign the dominant effect but certainly a small rotational barrier should be expected.

In the chromium complexes **6** and **7**, modeled by $(CO)_4Cr(CH_2)_2$ and $(CO)_4Cr(CHOH)_2$, the three conformations are found to be essentially isoenergetic. Therefore, no electronic preference is associated with the metal, and the carbene substituents can be turned in any manner to obtain the desired structure. In fact, the two carbenes are coplanar in the conjugated chelating ring while they are noticeably skewed when part of a nonconjugated chain.

In the molybdenum complex **4**, modeled by $(CO)_4Mo(C(NH_2)_2)_2$, (F,F) is found to be essentially isoenergetic with (E,F) while (E,E) is calculated to be considerably higher in energy for predominantly steric reasons. An examination of the conrotatory and disrotatory motions of the carbenes away from the (F,F) conformation has shown the maximum stabilization to be 1.6 kcal/mol with respect to (F,F), for a 45° conrotatory motion, in agreement with the experimental structure. Minimization of the steric hindrance seems to be responsible for this rotation and is probably underestimated since the models amino groups bear only H in place of the bulky real ligands. A related structure found for a d^6 ruthenium tetrakis(carbene) complex[5b] exhibits a similar steric influence.

Additional stabilization of the two carbene groups by making them part of an aromatic imidazole ring, as in **22**, does not modify our general conclusions. The carbene, in this case, can hardly be considered as a π-electron acceptor group (the MO diagram in ref 14c suggests in fact that the imidazole behaves more like a π-donor group). However, **22** adopts a conformation essentially equivalent to that of **4** in order to minimize steric hindrance.



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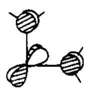
Other Systems with Other Electron Counts

We have just discussed the structures of some existing compounds in which the number of electrons at the metal varies from d^4 to d^8. Though d^2 and d^{10} bis(carbene) complexes have not, as far as we know, been characterized, we would like to suggest some plausible structures for them.

Complexes with a d^2 electron count have only one filled d orbital. The two carbene p_C orbitals might join force to stabilize this d orbital, causing the (F,F) conformation to be preferred (**11a**). Any added M–L/ligand interaction should reinforce this preference. Thus the (F,F) conformation should be preferred, independent of the metal or type of ancillary ligands.

The d^{10} complexes are more challenging. They are usually found to be tetracoordinate with either a tetrahedral, planar or some intermediate structure. The tetrahedral structure is preferred if the formal electron count is closer to d^{10} while a square-planar structure indicates an electron count closer to d^8 at the metal center. To analyze this, we have examined the conformations of the two carbenes in model tetrahedral and square-planar $H_2Pt(CH_2)_2^{2-}$. The three conformers of the tetrahedral structure are found significantly higher in energy than any of the square-planar ones. Among the planar isomers, the (E,E) structure is found to be more stable by 5.5 and by 7.4 kcal/mol than the (E,F) and (F,F) structures, respectively. The two electrons added to the classical d^8 situation (see above) must be housed in the antibonding metal–carbene orbital **23**. This would be extremely unfavorable without the availability, in the (E,E) conformer, of the empty metal p_z that can mix in a bonding manner, providing some extra stabilization (**24**). The other conformations, (E,F) and (F,F), do not have an equivalent low-lying metal p orbital available to stabilize the HOMO. These results reflect the π-accepting ability of the model carbene that reduces the formal d electron count to something less than d^{10}. Introduction of π-donor substituents on the carbenes may result in a preference for a tetrahedral structure. In that case the (F,F) conformation is the best candidate.



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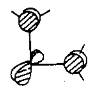

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The present study has mostly dealt with *cis*-bis(carbene) complexes with little approach to *trans*-bis(carbene). For nonstabilized carbenes, the conformation of a trans isomer should be mostly controlled by back-donation. The two carbenes should thus lie in orthogonal planes for any electron count different from d^2,[20] in which case, they should be coplanar. *trans*-Bis(carbene) complexes have been found to isomerize to the more stable cis isomer.[21] Unfortunately the understanding of the relative energies of *cis*- versus *trans*-bis(carbene) preference is rather hazardous with the EHT method because of the difficulty to estimate properly the trans effect. Our only attempt was thus restricted to the TBP case where the site preference was associated with the ligand field and not only with the trans effect.

Acknowledgment. We are grateful to Dr. J. Martin for a critical reading of the manuscript.

Appendix

All calculations were performed by using the extended Hückel method with the weighted H_{ij} approximation.[22] The atomic parameters which are given in Table IV are taken from previous literature.[23] The structural parameters are adapted from experimental structures. Pt complexes: Pt–C, 1.95 Å; Pt–Cl, 2.36 Å; Pt–H, 1.80 Å; C–O(CHOH), 1.44 Å. Ta complex: Ta–C, 1.90 Å; Ta–H, 1.72 Å. Rh complex: Rh–C, 2.02 Å; Rh–H, 1.70 Å; C–N(C(NH$_2$)$_2$), 1.33 Å; Rh–olefin midpoint, 2.08 Å; C–C(olefin), 1.42

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Å. Mo complex: Mo–C(O), 2.00 Å; C–O, 1.15 Å; Mo–C(carbene), 2.30 Å; C(carbene)–N, 1.33 Å; N–H, 1.00 Å; Mo–H, 1.70 Å. Cr complex: Cr–C(O), 1.84 Å; C–O, 1.14 Å; Cr–C(carbene), 2.00 Å; Cr–H, 1.6 Å; C–H, 1.08 Å. All angles at the metal are the ideal values characteristic of each ligand field. All angles within each ligand are standard.

Registry No. 1, 69552-43-8; 2, 71770-16-6; 3, 76748-17-9; 4, 64161-93-9; 5, 91463-01-3; 6, 78128-66-2; 7, 83288-64-6; $H_3Ta(CH_2)_2^{2-}$, 112069-47-3; $H_2Rh(CH_2)_2^-$, 112069-48-4; $(CO)_4Cr(CH_2)_2$, 110133-07-8; $(CO)_4Cr(CHOH)_2$, 112069-49-5; $(CO)_4Mo(C(NH_2)_2)_2$, 112137-50-5; $H_2Pt(CH_2)_2^{2-}$, 112069-50-8.

Molecular Orbital and Spectroscopic Studies of Triple Bonds between Transition-Metal Atoms. 3.[1] The d^5–d^5 Organometallic Dimer $Re_2(C_3H_5)_4$

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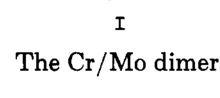
Received May 19, 1987

The valence electronic structure of the organometallic dimer $Re_2(\eta^3\text{-}C_3H_5)_4$ which formally has a Re–Re bond order of 3 has been investigated by using molecular orbital theory and photoelectron spectroscopy. Relativistic SCF–Xα–SW calculations have been performed on $Re_2(\eta^3\text{-}C_3H_5)_4$ and a Re–Re triply bonding electronic configuration of $\sigma^2\pi^4\delta^2\delta^{*2}$ was found in agreement with previous Xα calculations on the d^5–d^5 Re(II) dimer $Re_2Cl_4(PH_3)_4$ and Fenske–Hall calculations on the model system $Tc_2(allyl)_4$. The calculation clearly indicates that a substantial amount of metal to ligand π back-bonding is occurring, primarily via interaction of the filled Re δ and δ* orbitals with the energetically accessible allyl π* levels. The significant differences between the molecular structures observed for $M_2(allyl)_4$ (M = Cr, Mo) and $Re_2(allyl)_4$ most likely result from the electronic factors favoring increased π back-donation in the Re system. The He I photoelectron spectrum for $Re_2(\eta^3\text{-}C_3H_5)_4$ is presented, and assignments from the Xα–SW calculation are proposed. Comparisons with the photoelectron spectra for the isoelectronic Re(II) dimer $Re_2Cl_4(PMe_3)_4$ and the quadruply bonded molybdenum dimer $Mo_2(allyl)_4$ confirm the predicted Re–allyl π back-donation.

There has been a great deal of research directed toward understanding the synthetic chemistry, structure (molecular and electronic), and reactivities of transition-metal multiple bonds.[3] Although there is a very large number of dimers with metal–metal triple and quadruple bonds, the list of organometallic binuclear systems with multiple bonds is much smaller. The quadruply bonded octamethyldimetalate species, $M_2(CH_3)_8^{x-}$, have been characterized for chromium,[4] molybdenum,[5] tungsten,[6] and rhenium.[7] Another homoleptic series of organometallic compounds with quadruple M–M bonds are the $M_2(\mu_2,\eta^8\text{-}C_8H_8)(\eta^4\text{-}C_8H_8)_2$ cyclooctatetraene-based dimers which are known for M = Cr, Mo, and W.[8-10] All three molecules are essentially isostructural, with the Mo and W compounds being crystallographically isomorphous.

The first "all organometallic" dimer crystallographically characterized was dichromium tetraallyl, $Cr_2(C_3H_5)_4$, which was found to have two terminal and two bridging allyl ligands, and, although it was not recognized at the time, a M–M quadruple bond with a Cr–Cr separation of 1.98 (6) Å.[11] As with the other systems discussed above, the isostructural molybdenum system has also been prepared, while the tungsten analogue is, as yet, unknown.[12] Interestingly, there is a related Re(II) complex, $Re_2(\eta^3\text{-}C_3H_5)_4$, which has a $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configuration corresponding to a Re–Re triple bond. The rhenium complex, however, has a rather different molecular structure from that observed for the related Cr and Mo systems.[13] The structure of the Cr/Mo complex is shown schematically in I, while ORTEP plots of the $Re_2(\eta^3\text{-allyl})_4$ complex are given in Figure 1. The Cr/Mo dimers have two bridging



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