13.0 ppm (s, AsCH_3); minor isomer, 258.2 ppm (d, J = 41.4 Hz, C(O)CH_3), 207.2 ppm (d, J = 39.3 Hz, CO), 55.7 ppm (d, J = 9.5 Hz, P(OCH_3)), 51.6 ppm (s, C(O)CH_3), 13.4, 12.6 ppm (s, AsCH_3).

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Registry No. **8a**, 124379-93-7; **8b**, 124379-94-8; **8c**, 124379-95-9; **8d**, 124379-96-0; **8e**, 124399-61-7; **8f**, 124379-97-1; **8g**, 124379-98-2; **9a**, 124380-00-3; **9b**, 124380-02-5; **9c**, 124380-04-7; **9d**, 124380-06-9; **9e**, 124380-08-1; **9f**, 124380-10-5; **9g**, 124380-40-1; **15ag**, 124380-12-7; **15bg**, 124602-43-3; **15cg**, 124649-43-0; **15dg**, 124380-16-1; **15eg**, 124380-18-3; **15fg**, 124380-38-7; **15gg**, 124380-20-7; **15aa**, 124380-22-9; **15ba**, 124440-11-5; **15ca**, 124380-24-1; **15da**, 124380-26-3; **15ea**, 124380-28-5; **15ga**, 124440-05-7; **15fa**, 124380-30-9; **15gb**, 124649-43-0; **15ab**, 124380-32-1; **15bb**, 124380-34-3; **15db**, 124380-36-5; **15gd**, 124440-07-9; **15ad**, 124440-09-1; $P(OCH_3)_3$, 121-45-9; $PhP(OCH_3)_2$, 2946-61-4; $Ph_2P(OCH_3)$, 4020-99-9; $P(CH_3)_3$, 594-09-2; $PhP(CH_3)_2$, 672-66-2; Ph_2PCH_3, 1486-28-8; ETPB, 824-11-3; $(CH_3)_3NO$, 1184-78-7; iodosobenzene, 536-80-1.

Qualitative Molecular Orbital Studies of d^6 M(alkyne)$_2$L$_2$ and M(alkyne)$_3$L Complexes

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Qualitative molecular orbital arguments, supported by calculations at the extended Hückel level, are used in the analysis of the structure and bonding of d^6 M(alkyne)$_2$L$_2$ and M(alkyne)$_3$L complexes. In the former stoichiometry, the observed staggering is ascribed to an interaction between the alkyne $\pi_\perp$ orbitals and vacant orbitals on the metal. However, other structures with the alkynes coplanar are relatively low in energy by comparison, for a filled dπ–pπ conflict is avoided by the presence of a low-energy π-back-bond between orbitals that are formally vacant on the separated fragments. The tris(alkyne) stoichiometry has been discussed by others before; here a comparison is made between the observed C_{3v} structure and a structure with one of the alkynes rotated by 90°. The former is more stable because a filled $\pi_\perp$ orbital on the alkyne interacts with a combination on the other alkynes to create a rigorously nonbonding set. Such a masking is not available in the rotated structure. Both stoichiometries have marked asymmetries between the two ends of the alkyne ligand, as observed experimentally through bond distances or spectroscopic parameters. These can be explained in terms of corresponding asymmetries in the bonding to the two carbons.

Introduction

Alkynes are the only organic ligands in transition-metal chemistry that can, in principle, donate a variable number of electrons to a metal center without a change in the number of bound atoms. There are alkyne complexes known for almost all of the transition metals, and a firm consensus about their bonding to a metal, particularly a formally "electron deficient" metal, has been established.[1] Such bonding schemes are very important in the chemistry of mono(alkyne) complexes, and the literature contains examples of the reversible interconversion of four- and two-electron bonding modes on the coordination of an additional ligand[2] or the addition of two electrons to a metal center.[3] Poly(alkyne) complexes, for which possible conflicts and cooperation among the alkynes in π-donation and acceptance add an additional dimension of interest, form an important subgroup in the alkyne literature, with examples spanning almost the whole transition series. Among the studied poly(alkyne) stoichiometries are d^{10} M(alkyne)$_2$ (M = Pt[4]), d^4 M(alkyne)$_2$(O)X (M = Re[5]), M(alkyne)$_2$(η^5-cyclopentadienyl)X (M = Mo, W[6]), M(alkyne)$_2$(η^5-cyclopentadienyl)L (M = V, Nb, Ta[7]), d^4 M(alkyne)$_2$L$_2$X$_2$ (M = Mo, W[8]), and d^6 M(alkyne)$_2$L$_4$ (M = W[9]).

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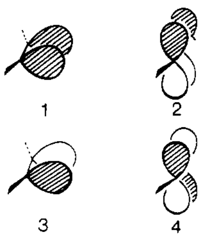

Figure 1. π orbitals for an alkyne ligand.

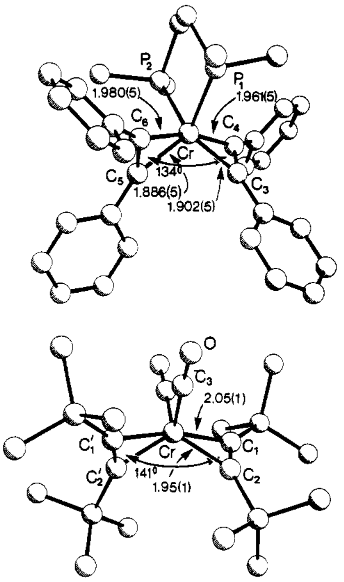

Figure 2. PLUTO drawings of Cr(Ph≡CPh)$_2$(dmpe)[15c] and Cr(Me$_3$SiC≡CSiMe$_3$)$_2$(CO)$_2$.[12a]

The study of all these molecules has been assisted by qualitative molecular orbital theory, usually supported by calculations at the extended Hückel level.[10]

Two important classes of poly(alkyne) complexes that have not been thoroughly studied theoretically are the d^6 complexes M(alkyne)$_3$X (M = Re[11]), M(alkyne)$_3$L (M = Cr,[12] Mo,[9b,13] W[14]), and M(alkyne)$_2$L$_2$ (M = Cr[3,12a,15]). In the tris(alkyne) case, qualitative MO theory has been invoked from the very first paper[14g] to explain why the *observed* C_{3v} geometry is stable. However, no consideration of alternate structures, which are certainly involved in fluxional processes, has been presented. The second stoichiometry is of considerably more recent vintage and represents the first time, to our knowledge, where two alkyne ligands donate *all* of the possible eight electrons to a metal. The present study seeks to develop a more comprehensive picture of the bonding of these poly(alkyne) complexes. It serves as an illustration of the importance of orbital conflicts and cooperativity for alkynes and emphasizes that, even where conflicts may arise, changes in orbital roles lower the energies of certain structures considerably.

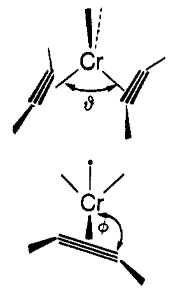

Figure 3. Definition of the angles θ, between the center of the alkynes and the metal, and φ, the torsional angle defined by the midpoint between the two CO ligands, the metal, the midpoint of the alkyne, and an alkyne carbon.

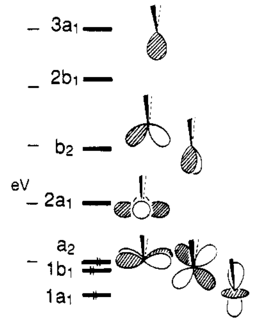

Figure 4. Frontier molecular orbitals for Cr(CO)$_2$. In addition to those illustrated, there are two orbitals of a_1 and b_2 symmetry involved in σ bonding with the CO's. These are located at lower energy.

The important ligand orbitals for metal–alkyne bonding are presented in Figure 1. One π orbital, 1, lies in the plane of the alkyne carbons and their immediate substituents and is commonly designated π-parallel ("$\pi_{\parallel}$"); it is always involved in alkyne–metal bonding, just as with the π system of an alkene ligand in the Dewar–Chatt–Duncanson model of olefin coordination.[16] The other π orbital, 2, is perpendicular to the first and may or may not interact with the metal ("$\pi_{\perp}$"). If this orbital can overlap with a vacant metal orbital, then the alkyne will donate more than two electrons to a metal. The antibonding components of the alkyne π orbitals, 3 and 4, can also be important, although any interactions of the $\pi_{\perp}$* orbital 4 with the metal will be of δ symmetry and therefore very small.

M(alkyne)$_2$(L)$_2$ Complexes

There are two crystallographically characterized complexes of the stoichiometry [M(alkyne)$_2$(L)$_2$] (Figure 2).[15] The paramount questions for our analysis of their structure and bonding concern the orientation of the alkyne ligands and the facility of alkyne rotation. We will vary two parameters in probing the alkyne orientations—the angle between the centers of the alkynes, θ, and the torsional angle for alkyne rotation, φ (Figure 3). In the experimental structures, the two alkyne ligands are moved well away from each other (θ_{av} = 137°) and are staggered (φ_{av}

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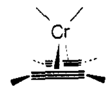
= 133°). In addition, there are much shorter bonds between the chromium and the *lower* carbons.

The starting metal fragment in this case is d^6 ML_2 with a set of frontier orbitals in the C_{2v} point group as shown in Figure 4,[17] with energies as calculated for $Cr(CO)_2$.[18] The most desirable geometry for the two alkynes will provide four filled ligand orbitals interacting with the LUMO's of the fragment while, if possible, maximizing the interactions of the π^* orbitals of the alkyne ligands with the filled metal orbitals.

The simplest pseudotetrahedral geometry for the bis(alkyne) complex places the two alkynes in mutually parallel positions, with φ = 90°, as in **5**. When θ = 90°, one of the symmetry-adapted combinations of the $\pi_\perp$ orbitals will be essentially nonbonding with respect to the metal (as discussed for pseudooctahedral complexes by Templeton).[1a] There is no metal orbital that will overlap well with the combination suggested in **6**.[19] A more complete interaction does occur if θ is allowed to increase, as in **7a**, to values greater than 100°. This, along with the other symmetry-allowed interaction **7b** and the two orbitals derived from the $\pi_\parallel$ orbitals **8a** and **8b**, means the two cis alkynes, even if parallel, *can* act as net eight-electron donors to the d^6 ML_2 fragment. If θ increases further, however, the calculated energy increases dramatically because of steric crowding and because the interaction suggested in **7b** decreases to zero.



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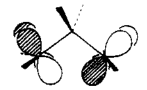

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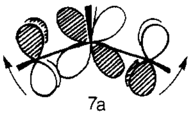

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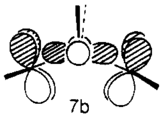
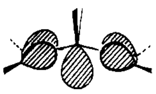


7b



8a

8b

The full interaction diagram for two cis parallel alkynes at θ = 130° is given in the top panel of Figure 5. The $\pi_\parallel$ orbitals transform as $a_1 + b_1$ and overlap well with the $3a_1$ and $2b_1$ orbitals on the fragment while the $\pi_\perp$ orbitals, which also transform as $a_1 + b_1$, will overlap with the $2a_1$ and the (formally occupied) $1b_1$ orbitals of the fragment. In this case the interaction of two formally filled fragment

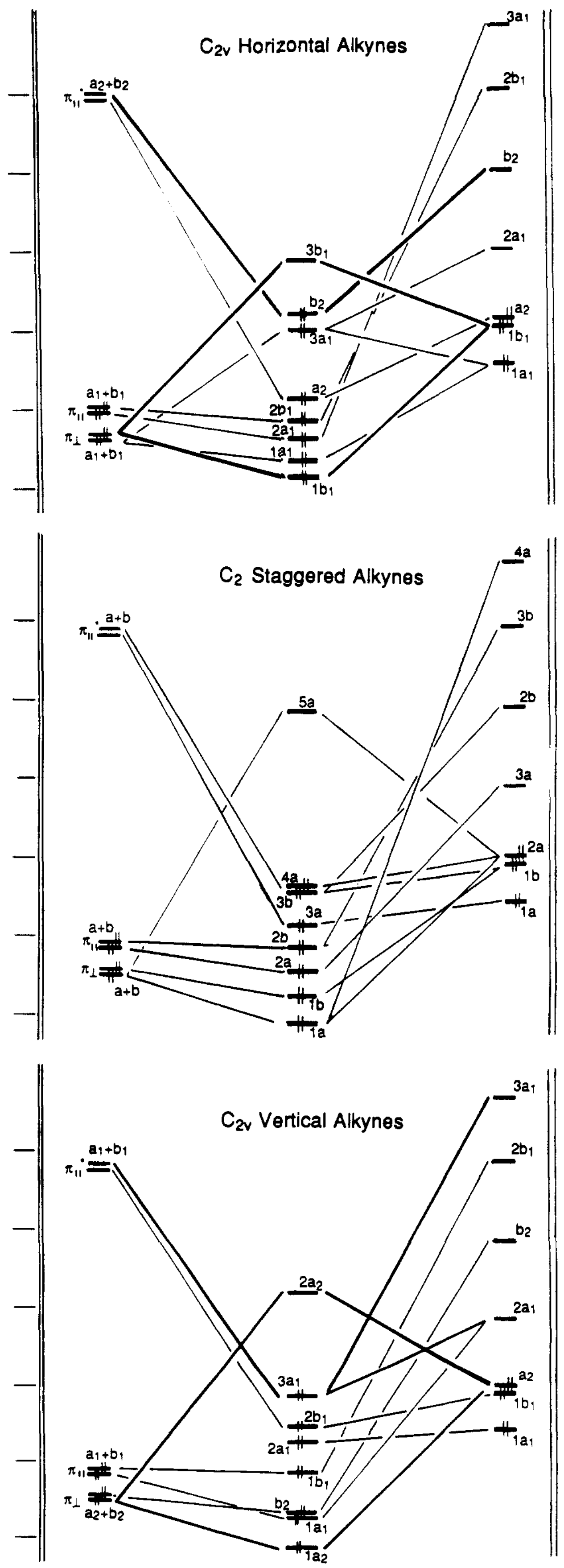


Figure 5. Major orbital interactions for the horizontal (φ = 140°, C_2), and vertical (φ = 180°, C_{2v} structures of $Cr(HC{\equiv}CH)_2(CO)_2$. The orbitals involved in the avoided $d\pi$–$p\pi$ conflict are highlighted in the two C_{2v} diagrams. Orbitals involving σ donation from the CO's to the metal are located at lower energy and are omitted.

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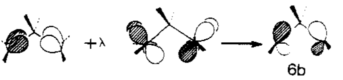
(18) The discussion in this paper is based on $Cr(CO)_2$, but we have confirmed that it also applies to complexes without π-acid ligands, such as the model complex $[Cr(HC{\equiv}CH)_2(H)_2]^{2-}$.

(19) It is interesting to note that this essentially ligand-centered orbital is actually a combination, permitted in this structure, of the $\pi_\parallel$ and $\pi_\perp$ orbitals. Another combination, **6b**, does get involved in an interaction with the metal.



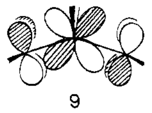
6b

Table I. Occupancy of Frontier Molecular Orbitals in $Cr(HC{\equiv}CH)_2(CO)_2$ at the Horizontal (φ = 90°), Staggered (φ = 140°), and Vertical (φ = 180°) Geometries

	φ		
orbital[a]	90°	140°	180°
$3a_1$	0.13	0.25	0.35
$2b_1$	0.20	0.22	0.19
b_2	0.91	0.31	0.18
$2a_1$	0.49	0.62	0.93 (LUMO in fragment)
a_2	1.35	1.05	0.59 (HOMO in fragment)
$1b_1$	0.50	1.35	1.52
$1a_1$	1.98	1.92	1.98

[a] The Mulliken symbols for the $Cr(CO)_2$ fragment are taken from the C_{2v} point group for comparison with Figure 4. Note that the point group in the staggered geometry (φ = 140°) is actually C_2.

orbitals does *not* result in a net antibonding situation in the complex, because the alkyne–metal antiboding $3b_1$ orbital is *vacant*—it is the molecule's LUMO, **9**. The HOMO of the complex is instead a π back-bonding orbital, $2b_2$ **10a**, formed by two orbitals of b_2 symmetry that are vacant in the fragments. Thus, there is a formal promotion of two electrons from the $1b_1$ to the b_2 orbital of the $Cr(CO)_2$ fragment. A second very good and more normal back-bond is formed between the alkynes' a_2 $\pi_\parallel^*$ combination and the fragment's filled a_2 orbital, **10b**.



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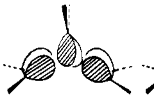
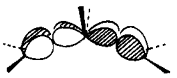
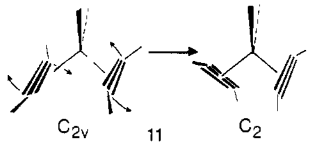


10a



10b

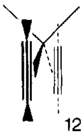
This analysis suggests that the cis parallel structure is consistent with an 18-electron $ML_2(alkyne)_2$ structure, with a possible conflict among filled orbitals avoided through the presence of a low-lying MO derived from formally unfilled orbitals. But a substantial stabilization—calculated to be about 17 kcal mol^{-1}—occurs if the alkyne ligands are staggered in a disrotatory fashion with preservation of the C_2 symmetry element (**11**). The energy minimum occurs at θ = 130° and φ = 140°, remarkably close to the experimental values.



11

The center panel of Figure 5 presents an interaction diagram for the most stable geometry, with labels appropriate for the C_2 point group. The additional stabilization occurs because the motion of the alkynes allows for better overlap in certain important orbital combinations. This geometry has no dπ–pπ conflicts, and there are two "genuine" π back-bonding orbitals, 3a and 3b, and two "genuine" $\pi_\perp$ donor orbitals, 1a and 1b, without any population of the corresponding antibonding orbitals. This is shown quantitatively by examining the calculated occupancies of the orbitals of the $Cr(CO)_2$ fragment, presented in Table I for φ = 90, 140, and 180° (we will come to the φ = 180°, or "vertical", case shortly). Note the depopulation of the filled $1b_1$ orbital at φ = 90° and the excess population of the originally vacant b_2 orbital. In the staggered case a more appropriate situation arises: the b_2 orbital now overlaps with filled ligand orbitals and can function as an acceptor, with a modest occupancy, while the $1b_1$ orbital can function as a π back-bonding orbital, with a small depletion of its original two electrons.

There is one other point on the C_2 structure surface to examine in detail: the case of φ = 180° (**12**). Here the alkynes lie vertically and the interaction diagram is as shown in the bottom panel of Figure 5. The energy at this geometry lies just 9 kcal mol^{-1} above the most stable staggered geometry and 8 kcal mol^{-1} below the parallel structure. It too is "compatible" with net eight-electron donation from the alkynes to the metal. Just as with the parallel case there is a filled–filled conflict between the a_2 $\pi_\perp$ combination and the occupied a_2 orbital on the $Cr(CO)_2$ fragment. But again a very good interaction between two unfilled orbitals becomes the molecular HOMO, $3a_1$, and, as indicated in Table I, there is a formal promotion of electron density from the occupied a_2 orbital to the unoccupied $2a_1$ orbital.



12

These arguments clarify the question of why the observed structures are stable. The close agreement between the calculated and observed structures increases our confidence in our conclusion that while there is ample opportunity for the important orbitals to overlap in any geometry, only in the staggered case are filled–unfilled interactions maximized. This analysis parallels that provided by Klein and co-workers for the staggered bis(olefin) configuration found for $Co(PMe_3)_2(C_2H_4)_2$ and $Fe(PEt_3)_2(C_2H_4)_2$.[20] There, the explanation is based on maximizing π back-bonding, while here we must consider the avoidance of dπ–pπ conflicts also.

Three quantitative details of the calculations deserve further note. First, some of the orbitals of the staggered complex—that closest to the experimental structures—contain very different contributions from the alkyne carbons distal and proximal to the CO's. The 4a orbital, **13**, is particularly asymmetric, with a negligible contribution on the upper carbons. As a result of this and other less dramatic asymmetries, there is more bonding electron density between the Cr and the lower carbons, resulting in a 20% greater overall reduced overlap population between the chromium and the lower carbons; the bonds to them are much stronger, as is indeed suggested by the Cr–C distances in the crystallographically studied complexes. This asymmetry on the alkynes is due to an allowed mixing of the $\pi_\parallel$ and $\pi_\parallel^*$ orbitals, as suggested in **14**.

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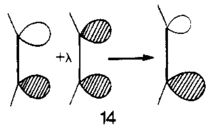

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(20) Klein, H.-F.; Helwig, M.; Koch, U.; Lull, G.; Tadic, M.; Krüger, C.; Hofmann, P. *Z. Naturforsch.* **1988**, *43B*, 1427. (b) Hoberg, H.; Jenni, K.; Angermund, K.; Krüger, C. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 153.

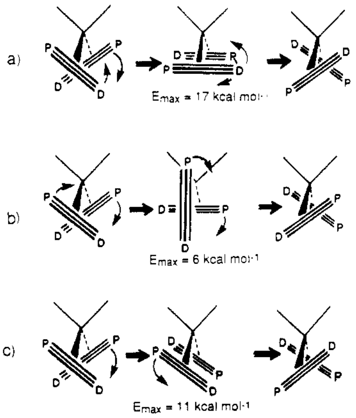


Figure 6. Alternate pathways for equilibration of the ends of the alkyne ligands. The highest energy point is indicated in the center, along with its energy with respect to the calculated ground state. P and D refer to positions proximal and distal to the L ligands at the start.

Second, the calculations discussed above show that a simple disrotatory motion through the parallel structure (Figure 6a) is plausible as a mechanism to interconvert the ends of the alkynes.[21] However, a conrotatory process (Figure 6b) is actually calculated to be more favorable, for here the staggering of the alkynes is preserved throughout the reaction coordinate. It is also possible to have rotation of a single alkyne at a time, at slightly higher calculated energy (Figure 6c). The last two mechanisms are both consistent with the fact that alkyne rotation cannot be frozen out.

A third detail concerns the electronic spectra of complexes with this stoichiometry. Both of the known complexes are deep red with absorption of most of the visible region. This is consistent with a structure lacking even a pseudo inversion center (so all transitions are allowed) and with a relatively small HOMO–LUMO gap, precisely what is found in our calculations, where even the most stable structure (φ = 140°) has a gap of just 2.2 eV, corresponding to a wavelength of ca. 5500 Å. However, it must be remembered that there is considerable "softness" in the structure, and other absorptions from geometries just slightly higher in energy may contribute significantly to the spectroscopy.

Finally, we are now in a position to speculate about the existence of other complexes of related stoichiometry. Earlier arguments emphasized that a full eight-electron donation requires a relatively large θ value and staggering. A complex with two more electrons—for example, the corresponding iron analogue—would only need six electrons donated. This can be achieved in a cis parallel structure (φ = 90°) with a relatively *small* θ, as suggested earlier. Indeed, the minimum-energy structure for the d^8 complex $[Cr(HC{\equiv}CH)_2(CO)_2]^{2-}$ is calculated to have parallel alkynes with θ = 105°, a point where there is a single orbital highly localized on the alkynes (**6**).[1a] This effectively hides the unneeded electrons, avoiding a dπ–pπ conflict.

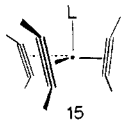
Table II. Rotational Barriers for M(alkyne)$_3$L Complexes[a]

complex	barrier, kcal mol^{-1}	ref
$[W(PhC{\equiv}CPh)_3(CO)]$	17.2	14a
$[NEt_4][W(PhC{\equiv}CPh)_4(SnPh_3)]$	13.1	14a
$[NEt_4][W(PhC{\equiv}CPh)_3(SnMe_3)]$	12.7	12a
$[W(PhC{\equiv}CPh)_3(PMe_2Ph)]$	16.4	12a
$[W(Me_3SiC{\equiv}CSiMe_3)_3(CO)]$	<8.0	12a
$[Cr(PhC{\equiv}CPh)_3(CO)]$	13.1	12a
$[Re(MeC{\equiv}CMe)_3CH_3]$	15	11

[a] In addition, the following complexes appear to be nonfluxional at any accessible temperatures: $W(EtC{\equiv}CEt)_3(CO)$, $Re(RC{\equiv}CR)_3I$ (R = Me, Et),[11] $[Re(MeC{\equiv}CMe)_3py]^+$.[11]

M(alkyne)$_3$(L) Complexes

The first poly(alkyne) complexes to be studied by qualitative molecular orbital methods were the tris(alkyne) complexes of tungsten, made by Tate and his co-workers over 25 years ago.[14g] They proposed a pseudotetrahedral geometry (**15**) on the basis of NMR evidence, and the structure was confirmed crystallographically by Bau[14d] in 1972. Other [M(alkyne)$_3$(L)] complexes have been made since then,[11-14] and several have been structurally characterized. All have the same C_{3v} geometry proposed by Tate, who also presented a symmetry-based argument as to why the stoichiometry adheres to the 18-electron rule. This discussion was presented more fully by King[14f] and indeed is a popular example of the utility of symmetry arguments in molecular orbital theory. The central point in the analysis is the fact that one of the symmetry-adapted linear combinations of the alkyne $\pi_\perp$ orbitals, which transforms according to the a$_2$ representation (**16**) has no match among the metal s, p, or d orbitals. The lone pair on L, three $\pi_\parallel$ orbitals on the alkynes, and two effective $\pi_\perp$ orbitals donate 12 electrons to the d^6 metal.



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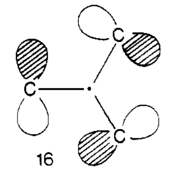

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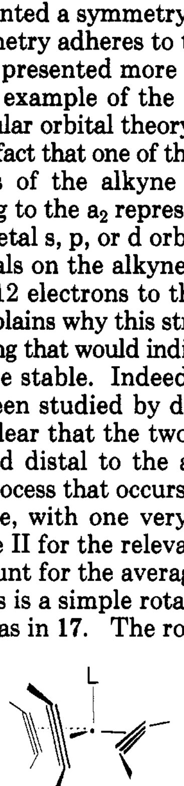
This argument explains why this structure is stable, but it is devoid of anything that would indicate why some other structure is not more stable. Indeed, several complexes of this type have been studied by dynamic NMR spectroscopy, and it is clear that the two ends of the alkyne ligand, proximal and distal to the apical ligand L, are averaged by some process that occurs at about the rate of the NMR time scale, with one very sterically crowded exception (see Table II for the relevant data). The most obvious way to account for the averaging of the two ends of the alkyne ligands is a simple rotation through a staggered intermediate, as in **17**. The rotation of the alkyne in this case is defined by the angle ω (**18a**). In addition, we will refer to the angle formed from the apical ligand



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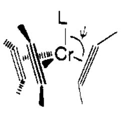
18a



18b

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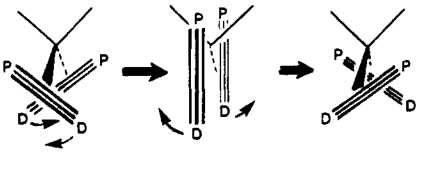
(21) Note that the corresponding disrotatory process through a vertical geometry would *not* interconvert the ends of the alkynes:



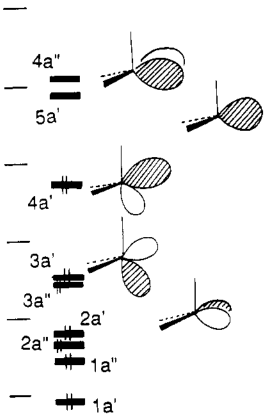


Figure 7. Frontier molecular orbitals for Cr(HC≡CH)$_2$(CO) in the C_s point group.

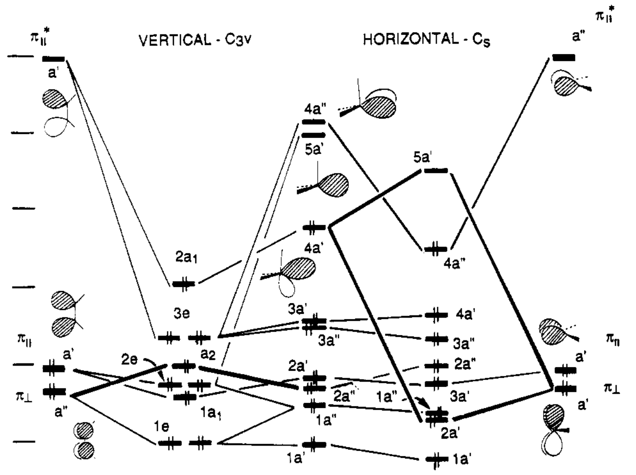


Figure 8. Orbital interaction diagram for Cr(HC≡CH)$_2$(CO) with a third vertical (ω = 0°) and horizontal (ω = 90°) alkyne. For the vertical case, symmetry labels for the C_{3v} point group are given and the ligand–metal nonbonding orbital is highlighted. For the horizontal case, the orbitals involved in the "avoided" dπ–pπ conflict are highlighted.

L to the metal to the center of the alkyne ligand, ψ (**18b**).

It is necessary to perform a quantitative calculation to explain the preferred geometry. First, the calculations indicate that the most stable geometry is that observed experimentally, with ψ ca. 105° and all the alkyne ligands parallel (ω = 0°).[22] But what about the rotation of a single alkyne? We treat the problem from the point of view of the interaction between the M(alkyne)$_2$L fragment and the alkyne ligand. Consider first the orbitals of the metal fragment (Figure 7). There are eight occupied orbitals that involve the metal (one, primarily a σ-donor interaction from the apical ligand L, lies at much lower energy and is omitted); it is a 16-electron fragment. The LUMO 5a′ is a σ acceptor and will interact with the alkyne $\pi_\parallel$ orbital, essentially independent of orientation. The other orbitals can enter into either π-acceptor or π-donor interactions with the alkyne.

Figure 8 contains an orbital interaction diagram for vertical (ω = 0°) and horizontal (ω = 90°) geometries. The vertical structure is preferred, and almost by inspection one can see that the $\pi_\parallel$* orbital of the alkyne can interact well with the two highest occupied fragment orbitals on the metal portion. Perhaps more importantly, the $\pi_\perp$ orbital on the third alkyne contributes to the create the π-donor set 1e and the nonbonding a$_2$ orbital. This latter orbital serves, ultimately, to "hide" $\pi_\perp$ on the third alkyne from any filled–filled conflicts.

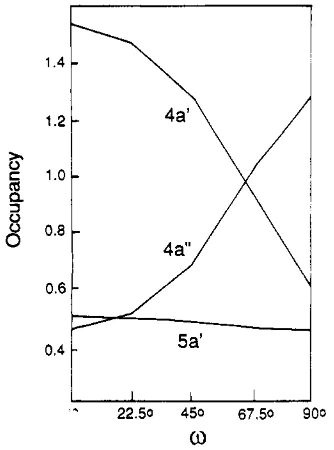
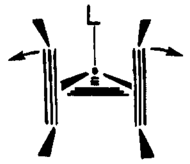


Figure 9. Variation in the calculated occupancies of the frontier orbitals of the M(alkyune)$_2$L fragment with ω.

The horizontal geometry is destabilized because it cannot hide the $\pi_\perp$ orbital. Instead, there is a simple dπ–pπ conflict between it and the fragment's filled 4a′ orbital. This is similar, in principle, to the case of an alkyne bound to a 16-electron octahedral fragment, such as with W(CO)$_3$(dppe)(HCCR).[9b] The horizontal geometry does nonetheless avoid filling a metal–ligand antibonding orbital because, as with the bis(alkyne) complexes, the antibonding orbital formed by the dπ–pπ conflict is (Figure 8) the molecular LUMO 5a′; a very good π back-bond is formed by two formally vacant orbitals. Because of this, the calculated energy of the horizontal structure is only 24 kcal mol^{-1} above that of the most stable structure. The effect of the avoided dπ–pπ conflict can be seen in comparing the occupancies of the frontier orbitals of the M(alkyne)$_2$L fragment as ω is varied for the third alkyne. Figure 9 contains a plot of the occupancies of the HOMO 4a′ and the two LUMO's 5a′ and 4a″. Note that, at the most stable geometry (ψ = 0°), there is a modest population of the previously vacant 5a′ and 4a″ and partial depopulation of the fragment HOMO 4a′, a result of backbonding. However, the rotation causes the 4a′ and 4a″ orbitals to switch roles: the 4a″ orbital is more heavily populated—it is part of the 4a″ HOMO in the ω = 90° case. Meanwhile, the 4a′ orbital of the fragment becomes substantially *de*populated, not because there is a π back-bond but because it is now essentially a mere acceptor orbital—engaged in the π-donor orbital of the molecule, 2a′ (Figure 8).

Steric relief also contributes to the reduction of the rotational barrier. The energy of the rotated structure drops to ca. 20 kcal mol^{-1} if the two *unrotated* alkynes are allowed to move a few degrees, as in **19**. This relieves some of the crowding between the axial ligand and the proximal carbons. The experimental data in Table II indeed indicate, fairly consistently, that an increase in crowding *and*



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[22] In their first paper, Tate and Augl pointed out that the NMR data were also consistent with a skewed structure, which would have ω deviating slightly from 0°.

Table III. Chemical Shift and Coupling Constant Data for Selected [M(alkyne)$_3$L] Complexes[a]

complex	proximal C δ	proximal C $^3J_{X-C}$, Hz	distal C δ	distal C $^3J_{X-C}$, Hz	ref
[NEt$_4$][W(PhC≡CPh)$_3$(SnMe$_3$)] (a)	186.9	104	196.1	23	12a
[NEt$_4$][W(PhC≡CPh)$_3$(SnPh$_3$)] (b)	183.3	107	197.3	35	14a
[W(PhC≡CPh)$_3$(PMe$_2$Ph)] (c)	180.4	19	197.7	4	12a
[W(PhC≡CH)$_3$(PMe$_3$)] (d)	164.2	15	201.4	5	14b
[W(PhC≡CH)$_3$(PPh$_3$)] (e)	167.1	40	199.7	4	12a
[W(PhC≡CPh)$_3$(CO)] (f)	174.4		192.5		14a
[Cr(PhC≡CPh)$_3$(CO)] (g)	181.7		203.9		12a
[Re(MeC≡CMe)$_3$I] (h)	157.1		168.2		11
[Re(MeC≡CMe)$_3$Me] (i)	163.7		177.8		11
[Re(EtC≡CEt)$_3$I] (j)	162.8		171.8		11
[Re(MeC≡CMe)$_3$py][SbF$_6$] (k)	158.7		181.2		11

[a] For complexes a–e, chemical shift assignments are made by observation of coupling to the apical atom, in comparison with the data for [W(PhC≡CH)$_3$(PMe$_3$)], which has been structurally characterized. For complexes f–k, assignments are made on the basis of the absolute trend in the other complexes to have the proximal carbon at *higher* field.

Table IV. Parameters for Extended Hückel Calculations

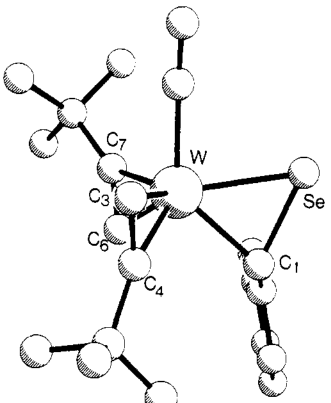
orbital	H_{ii}, eV	ζ_1	ζ_2	C_1	C_2
Cr 3d	−11.22	4.95	1.60	0.4876	0.7205
4s	−8.66	1.70			
4p	−5.24	1.70			
C 2s	−21.40	1.625			
2p	−11.40	1.625			
O 2s	−32.30	2.275			
2p	−14.80	2.275			
H 1s	−13.60	1.30			

electron density on the metal lowers the rotational barrier, perhaps by emphasizing the benefit of the motion suggested in **19** (steric control) or by altering the electron distribution in the transition state.[11]

Several orbitals in the C_{3v} structure are remarkably asymmetric with respect to the alkyne carbons. The degenerate π-acceptor set 3e and the σ-donor orbital 1a$_1$ are particularly concentrated on the upper and lower carbons, respectively. In the present case the asymmetries do not apparently result in a noticeable difference in total bonding between the metal and the two ends of the alkyne ligand, and indeed the published structures show that alkyne bonding is quite symmetrical. However, the calculated asymmetries do suggest an explanation for the interesting spectroscopic differences that have been noted in these molecules.

Table III presents the data for chemical shift and coupling constants that have been observed for several complexes. The chemical shift differences are significant and consistent, suggesting that the two positions are quite different electronically. Also, the coupling to the pseudo-cis proximal carbon (apical–metal–proximal angle 80 ± 5°) is much larger than that to the pseudo-trans (angle 125 ± 5°) carbon. The reasons for this undoubtedly lie in the intimate nature of the coefficients of the various atomic orbitals within the molecular orbitals, for it is likely in these systems that the Fermi contact term will dominate the coupling.

Finally, it is interesting to compare this analysis of the frontier orbitals of M(alkyne)$_2$L with the structures of the thio- and selenoaldehyde complexes W(HC≡CCMe$_3$)$_2$(CO)(X=C(Ph)H) reported by Fischer, Alt, and their coworkers.[23] These provide a subtle test of accuracy of the calculated orbital diagram for the M(alkyne)$_2$(L) fragment. Its σ-acceptor orbital, 5a′, is heavily oriented toward the position *proximal* to the CO. One would expect the better donor atom on X=C(Ph)H to go to the proximal position, and that is the preferred, though not the only, orientation experimentally observed, as in **20**.



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Appendix

All quantitative data were obtained from calculations performed by using the extended Hückel method[10] with the modified Wolfgang–Helmholtz procedure.[24] Parameters, taken from Albright et al.,[25] are listed as in Table IV. The alkyne geometries were set with a C–C bond of 1.30 Å and a C–C–H angle of 150°; a fixed distance of 1.90 Å from Cr to the midpoint of the alkyne bond was used. The C–O bond distance was fixed at 1.20 Å and the Cr–C(O) distance at 1.75 Å.

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