

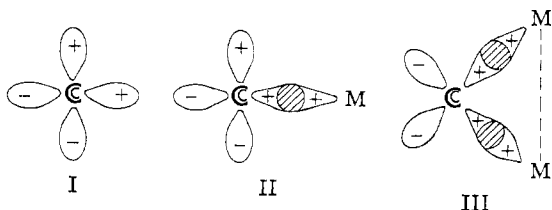
# Correspondence

## The Nature of the Tris(alkyne)tungsten Monocarbonyls and Related Complexes<sup>1</sup>

Sir:

Among the most perplexing of the products formed by the reactions between alkynes and metal carbonyls are the compounds  $(RC_2R')_3WL$  ( $R = R' = C_2H_5$  or  $C_6H_5$ ,  $L = CO$ ;<sup>2</sup>  $R = R' = CF_3$ ,  $L = CH_3CN$ <sup>3</sup>) obtained by reactions between  $(CH_3CN)_3W(CO)_3$  and various alkynes. A few molybdenum analogs<sup>4,5</sup> are also known. Despite the availability of these complexes for several years, no convincing explanation of their peculiar but well-established stoichiometry has appeared. Even the molecular orbital treatment in the first full paper<sup>2</sup> on these complexes does not clarify this point. With three apparently equivalent acetylene ligands one might have expected a stoichiometry of either  $(RC_2R')_3WL_3$  or  $(RC_2R')_3W$  rather than  $(RC_2R')_3WL$ . It has now been found that a very elementary application of molecular orbital and group theory demonstrates the reason for the apparently unusual formulas of these complexes.

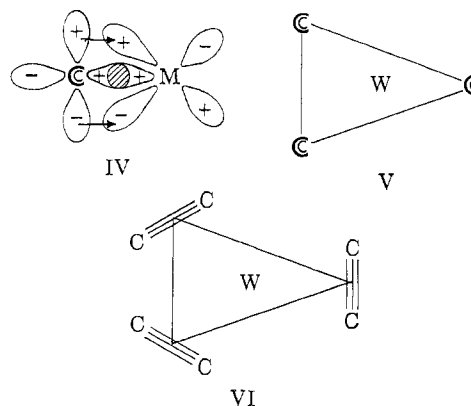
The carbon-carbon triple bond of an alkyne molecule contains two orthogonal  $\pi$  bonds. Let us now consider solely the filled bonding orbitals of these orthogonal  $\pi$  bonds represented schematically by structure I looking down the carbon-carbon axis.



Three modes of the bonding of such an alkyne ligand to a metal are possible.<sup>6</sup> In the first of these modes of bonding (monodentate monometallic) depicted in II one of the filled molecular orbitals forms a  $\sigma$  bond with a metal hybrid orbital. The other filled molecular orbital is not involved in the bonding to the metal atom. The alkyne-metal bond is thus very similar to an olefin-metal bond. Examples of alkyne-metal bonds of this type are found in complexes of the type  $C_5H_5Mn(CO)_2(alkyne)$ .<sup>7</sup> In these complexes the mono-

dentate monometallic alkyne ligand acts as a two-electron donor.

The second type of alkyne-metal bonding (bidentate bimetallic) is depicted schematically in III. In this case each of the filled molecular orbitals forms a  $\sigma$  bond with a metal atom. A complex with two metal atoms is thus obtained. In most such complexes a metal-metal bond is also present between the two metal atoms. Examples of bidentate bimetallic alkyne-metal bonding are found in complexes of the types  $(alkyne)Co_2(CO)_6$ <sup>8</sup> and  $(alkyne)Ni_2(C_5H_5)_2$ .<sup>9</sup>



The third type of alkyne-metal bonding (bidentate monometallic) is depicted schematically in IV. This is the type of alkyne-metal bonding which has not been previously recognized and the one that is important to consider when discussing the  $(alkyne)_3WL$  complexes. In bidentate monometallic alkyne-metal bonding one of the filled molecular orbitals of the alkyne ligand forms a  $\sigma$  bond with a metal hybrid orbital. The other perpendicular filled molecular orbital of the alkyne ligand is of suitable symmetry to form a  $\pi$  bond with an empty metal d orbital. This type of  $\pi$  bonding results in the forward donation of an electron pair from the ligand to the metal atom in contrast to the more frequently encountered retrodonative  $\pi$  bonding (found in metal complexes of olefins, phosphines, carbon monoxide, etc.) which results in partial donation in the other direction of an electron pair from the metal atom to the ligand. When bonded to a metal atom in this bidentate monometallic manner an alkyne donates four electrons to the metal atom.

The most stable metal complexes have the metal atom in the rare gas electronic configuration. In the case of a tungsten complex a neutral tungsten atom requires a total of 12 electrons from the surrounding ligands to attain this favored electronic configuration. A complex of the type  $(alkyne)_3W$  with all three alkyne ligands of the four-electron-donor bidentate monometallic type would have this favored electronic con-

(1) The author is indebted to the Petroleum Research Foundation of the American Chemical Society for partial support of this work under Grant No. 2838-A1,3.

(2) D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Am. Chem. Soc.*, **86**, 3261 (1964).

(3) R. B. King and A. Fronzaglia, *Inorg. Chem.*, **5**, 1837 (1966).

(4) W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, **19b**, 959 (1964).

(5) R. B. King, *J. Organometal. Chem.* (Amsterdam), **8**, 139 (1967).

(6) This paper considers solely the dative ("forward") bonding between the alkyne ligand and the metal atom. Possibilities for supplementary retrodonative ("backward") bonding between the alkyne ligand and the metal atom also exist but are neglected in this elementary discussion.

(7) W. Strohmeier and D. von Hobe, *Z. Naturforsch.*, **16b**, 402 (1961).

(8) H. W. Sternberg, H. Greenfield, R. A. Friedel, J. Wotiz, R. Markby, and I. Wender, *J. Am. Chem. Soc.*, **76**, 1457 (1954).

(9) J. F. Tilney-Bassett, *J. Chem. Soc.*, 577 (1961).

figuration. However, it will now be shown that three alkyne ligands cannot be simultaneously bonded to a metal atom in this manner.<sup>10</sup> This is a simple problem since it is identical with previous  $\pi$ -bonding hybridization problems well worked out in cases such as oxy anions.<sup>11</sup>

Two configurations for a hypothetical (alkyne)<sub>3</sub>W molecule must be considered. In the first such configuration ( $D_{3h}$ ) the centers of the alkyne ligands are in the same plane as the central tungsten atom. In the second less symmetrical case ( $C_{3v}$ ) the centers of the alkyne ligands are in a plane not containing the central tungsten atom. In both the  $D_{3h}$  and  $C_{3v}$  cases the carbon-carbon triple bonds of the alkyne ligands can be oriented in two different manners relative to the remainder of the molecule. In the case depicted schematically in V for the  $D_{3h}$  configuration the carbon-carbon triple bonds are perpendicular to the plane containing the tungsten atom and ligand centers. This places the orbitals of the alkyne forming the dative  $\pi$  bond with the metal atom in the same plane as the tungsten atom and ligand centers. In determining the tungsten orbitals which could form this dative  $\pi$  bond, the  $\pi(\parallel)$  orbitals must thus be considered. In the alternative case depicted schematically in VI the carbon-carbon triple bonds are in the same plane as the tungsten atom and ligand centers. This places the orbitals of the alkyne forming the dative  $\pi$  bond with the metal atom perpendicular to the plane containing the tungsten atom and ligand centers. In determining the tungsten orbitals which could form this dative  $\pi$  bond the  $\pi(\perp)$  orbitals must thus be considered.

A closer inspection of the case depicted in VI for the  $D_{3h}$  configuration reveals severe steric hindrance between the R groups attached to the carbon-carbon triple bonds. This steric factor makes the case depicted in VI involving  $\pi(\perp)$  orbitals unfavorable relative to the case depicted in V involving  $\pi(\parallel)$  orbitals. Furthermore, in the case depicted in VI the six carbon atoms of the three carbon-carbon triple bonds are excellently situated for the three alkyne ligands to trimerize into the corresponding benzene derivative with concurrent destruction of the complex.<sup>12</sup> Thus there are ample reasons to believe that the case depicted in VI is unstable for steric reasons and need not be considered further. Therefore for the  $D_{3h}$  configuration only the case depicted in V involving  $\pi(\parallel)$  orbitals need be considered.

The representation  $\Gamma_{\pi(\parallel)}$  for this case (V) can easily be reduced to the irreducible representations<sup>13</sup>  $A_2' + E'$ . There are no metal orbitals of the available s, p,

and d types corresponding to the  $A_2'$  representation. The ( $p_x, p_y$ ) and ( $d_{xz-y^2}, d_{xy}$ ) sets of metal orbitals<sup>14</sup> correspond to the  $E'$  representation. Thus there are only two appropriate metal orbitals available to receive electron pairs by dative  $\pi$  bonding from the orbitals of the three alkyne ligands. This means that only two of the three alkyne ligands can bond to the tungsten atom as bidentate ligands; the third alkyne ligand must bond to the metal atom only as a monodentate ligand.

The less symmetrical  $C_{3v}$  configuration can be treated exactly like the  $D_{3h}$  configuration. Again the case involving the  $\pi(\perp)$  orbitals can be rejected as unlikely since the ends of the three alkyne ligands are too close together. The representation  $\Gamma_{\pi(\parallel)}$  for the  $C_{3v}$  case can be reduced to the irreducible representations  $A_2 + E$ . Again there are no metal orbitals of the available s, p, and d types corresponding to the  $A_2$  representation. The ( $d_{xz-y^2}, d_{xy}$ ) and ( $d_{xz}, d_{yz}$ ) sets of metal orbitals<sup>15</sup> correspond to the E representation. Thus in the  $C_{3v}$  configuration as in the more symmetrical  $D_{3h}$  configuration there are only two appropriate metal orbitals available to receive electron pairs by dative  $\pi$  bonding from the orbitals of the three alkyne ligands.

This treatment indicates that in (alkyne)<sub>3</sub>M complexes only two of the three alkyne ligands can be bidentate four-electron donors; the third alkyne ligand can be only a monodentate two-electron donor. Furthermore, it can be shown that the  $\sigma$  bonding between the three alkyne ligands and the metal atom for either the  $D_{3h}$  case (V) or the  $C_{3v}$  case does not preempt any of the metal orbitals required for the  $\pi$  bonding of the two bidentate four-electron donor alkyne ligands. In the  $D_{3h}$  case the representation  $\Gamma_{\sigma}$  can be reduced to the irreducible representations  $A_1' + E'$ . Similarly in the  $C_{3v}$  case the representation  $\Gamma_{\sigma}$  can be reduced to the irreducible representations  $A_1 + E$ . In both cases the only irreducible representation common to both the  $\sigma$  and the  $\pi$  bonding is the E-type representation. In both cases there are at least two different pairs of metal orbitals transforming as this E-type representation; therefore, one pair is available for the  $\sigma$  bonding and another pair is available for the  $\pi$  bonding.

This treatment shows that in an (alkyne)<sub>3</sub>W unit of either  $D_{3h}$  or  $C_{3v}$  symmetry, the three alkyne ligands can donate a total of only ten electrons to the tungsten atom leaving it two electrons short of the favored rare gas configuration. One way for an (alkyne)<sub>3</sub>W unit to attain the rare gas configuration would be by addition of a single monodentate ligand to supply the remaining two electrons; this apparently is the cause for the prevalence of (alkyne)<sub>3</sub>WL complexes.

This model of the bonding in the (alkyne)<sub>3</sub>W unit results in two bidentate four-electron-donor alkyne

(10) This statement contains the implicit assumption that metal s, p, d, but not f orbitals are involved in the bonding in complexes of this type. In support of this assumption there is no evidence for involvement of the metal f orbitals in the bonding in transition metal organometallic compounds.

(11) For illustrations of this simple technique applied to the  $\pi$  bonding in various oxy anions see F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, pp 98-107.

(12) Another possible alternative configuration of an (alkyne)<sub>3</sub>W species has the three alkyne ligands bridging *cis* positions of an octahedron with the tungsten atom in the center. This configuration has  $C_2$  symmetry like the  $[\text{Co}(\text{en})_3]^{3+}$  cation. In this configuration the ends of the three alkyne ligands are well situated for trimerization into a benzene derivative. It can therefore be excluded from present consideration.

(13) The problem is identical with that of  $\text{BF}_3$  or  $\text{NO}_3^-$  discussed in ref 11, pp 101-102.

(14) The z axis is assumed to be perpendicular to the plane containing the tungsten atom and the three ligand centers.

(15) The z axis in this configuration is identical with the  $C_3$  axis.

ligands and one monodentate two-electron-donor alkyne ligand. However, the actual structure of the  $(\text{alkyne})_3\text{W}$  unit may be regarded as a resonance hybrid with three canonical forms involving the various permutations of two bidentate and one monodentate alkyne ligands. All alkyne ligands in the  $(\text{alkyne})_3\text{W}$  unit are thus equivalent. Each one donates  $3^{1/3}$  electrons to the tungsten atom. This resonance effect is very similar to the effect making all carbon-carbon bond distances equal in benzene. The equivalence of all three alkyne ligands in the  $(\text{alkyne})_3\text{WL}$  complexes as demonstrated by nmr studies is consistent with this model of the bonding in the  $(\text{alkyne})_3\text{W}$  unit.

Compounds with bidentate monometallic alkyne ligands appear to be rare outside the series  $(\text{alkyne})_3\text{ML}$  ( $\text{M} = \text{Mo}$  or  $\text{W}$ ;  $\text{L} = \text{CO}$  or  $\text{CH}_3\text{CN}$ ). Possible other candidates are compounds of the type  $\text{C}_3\text{H}_5\text{M}(\text{CO})_2$ - $(\text{alkyne})$  ( $\text{M} = \text{V}^{16}$  or  $\text{Nb}^{17}$ ) where the central metal atom requires four electrons from the alkyne ligand to attain the favored rare gas configuration. A major ob-

stacle to the synthesis of a wide range of bidentate monometallic alkyne derivatives lies in the tendency for alkynes to condense together into benzene, cyclobutadiene, cyclopentadienone, tropone, or other more complex organic derivatives which sometimes then  $\pi$  bond to the metal atom. In most systems this alkyne condensation reaction occurs much more easily than either monodentate or bidentate  $\pi$  bonding of a single alkyne ligand to a single metal atom. Some possible synthetic routes to new types of alkyne-metal complexes with bidentate monometallic ligands are under exploration in this laboratory.

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(17) A. N. Nesmeyanov, K. N. Anisimov, N. E. Kolobova, and A. A. Pasynskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 774 (1966).

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RECEIVED OCTOBER 9, 1967