

complexes is slightly in favor of the azide ion, showing that N_3^- is a better nucleophilic reagent than is Cl^- .

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Novel Acetylene Tungsten Carbonyl Complexes

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Disubstituted alkynes such as 3-hexyne, diphenylacetylene, and methylphenylacetylene react with tris(acetonitrile)tungsten tricarbonyl or mono(acetonitrile)tungsten pentacarbonyl to give $(RC\equiv CR)_3W(CO)$. The structure and a qualitative molecular orbital picture are discussed. Similar reactions with the trisacetonitrile complexes of chromium and molybdenum cause cyclization to give hexaalkylbenzene or tetraphenylcyclopentadienone. Monosubstituted acetylenes do not give identifiable products under comparable reaction conditions. The reaction of stilbene with mono(acetonitrile)tungsten pentacarbonyl gives a normal olefin complex, mono(stilbene)tungsten pentacarbonyl.

Introduction

Metal carbonyls can react with alkynes to give one of three general types of complexes: (1) the alkynes might cyclize with formation of a homocyclic ring system such as cyclobutadiene derivatives,¹⁻⁴ benzene derivatives,⁵⁻⁷ cyclic ketones such as cyclopentadienones, quinones, and tropones,^{2,3,8-14} or with formation of heterocyclic rings^{13,15-17}; (2) the alkyne acts as a dinuclear bridging ligand^{2,3,18-22}; and (3) the alkyne is bonded to a single transition metal atom without ring formation. Only a very few compounds of the latter type are reported in the literature.²³⁻³⁰

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We recently reported the preparation of a new acetylenic complex of tungsten that appears to be of the latter type.³¹ This study has now been extended to other alkynes and the other subgroup VIB metals.

Experimental

$(CH_3CH_2C\equiv CCH_2CH_3)_3W(CO)$ (I) was prepared as described in an earlier publication.³¹

$(C_6H_5C\equiv CC_6H_5)_3W(CO)$ (II).—Diphenylacetylene (4.5 g.) and $(CH_3CN)_3W(CO)_3$ (3.3 g.) in 55 ml. of ethanol were refluxed under nitrogen for 18 hr. Carbon monoxide was evolved (about 380 cc.) (calcd. for 2 equiv., 422). The pale yellow crystals (5.2 g.) were collected, taken up in benzene, and precipitated with ethanol giving $(C_6H_5C\equiv CC_6H_5)_3W(CO)$, m.p. 193°, color change around 175°.

Anal. Calcd. for $C_{28}H_{20}OW$: C, 69.25; H, 4.03; W, 24.67; mol. wt., 746. Found: C, 69.77, 69.96; H, 4.34, 4.21; W, 24.55; mol. wt., 754 (osmometer, benzene).

This compound may be made similarly starting with diphenylacetylene and $(CH_3CN)_3W(CO)_3$. It can also be prepared by simply heating the reactants to 70° under vacuum without solvent for a few hours.

$(CH_3C\equiv CC_6H_5)_3W(CO)$ (III).—Methylphenylacetylene (10 ml.) and $(CH_3CN)_3W(CO)_3$ (3.9 g.) were heated to 90° with stirring under reduced pressure (195 mm.). Gas evolution ceased within 1 hr. The pressure was then lowered to 5 mm. and the excess methylphenylacetylene distilled off at 90°. The brown viscous residue was taken up in 8 ml. of ether and filtered. This solution was added to 80 ml. of methanol. Dropwise addition of water precipitated light yellow crystals which on crystallization from benzene gave $(CH_3C\equiv CC_6H_5)_3W(CO)$, m.p. 96–98°.

Anal. Calcd. for $C_{28}H_{24}OW$: C, 60.02; H, 4.32; W, 32.81; mol. wt., 560. Found: C, 60.3; H, 4.3; W, 33.4; mol. wt., 564 (osmometer, benzene).

Oxidation with excess I_2 in refluxing ethanol evolved 0.97 equiv. of CO based on a molecular weight of 560. Methylphenylacetylene could be recovered from a Dry Ice trap after pyrolyzing this compound under vacuum.

$(C_6H_5CH=CHC_6H_5)_3W(CO)_3$.—A mixture of *trans*-stilbene (0.6 g.) and $(CH_3CN)_3W(CO)_3$ (1.0 g.) was heated to 130° under good vacuum until gas evolution ceased. The black residue was extracted with benzene and the benzene solution evaporated to dryness. The orange-red solid was crystallized from hexane-benzene to give (stilbene) $W(CO)_3$, m.p. 135°.

Anal. Calcd. for $C_{19}H_{12}O_3W$: C, 45.25; H, 2.38. Found: C, 45.27, 45.24; H, 2.82, 2.68.

Nuclear Magnetic Resonance Spectra.—Proton magnetic resonances were observed with a fully equipped Varian DP-60

(29) S. V. Bukhovets and K. A. Molodova, *Zh. Neorgan. Khim.*, **2**, 776 (1957); *ibid.*, **3**, 1540 (1958).

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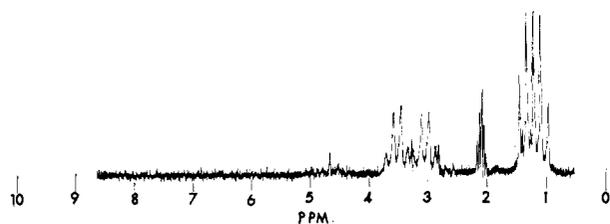


Fig. 1a.—Nuclear magnetic resonance spectrum of tris(diethylacetylene)tungsten carbonyl $(C_2H_5C\equiv C_2CH_5)_3W(CO)$.

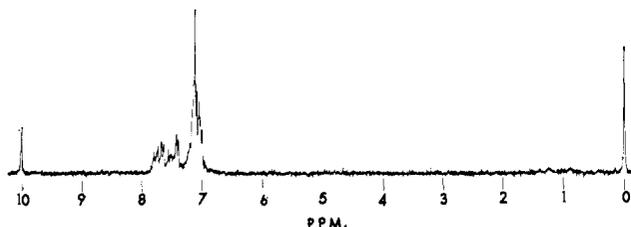


Fig. 1b.—Nuclear magnetic resonance spectrum of tris(diphenylacetylene)tungsten carbonyl $(C_6H_5C\equiv CC_6H_5)_3W(CO)$.

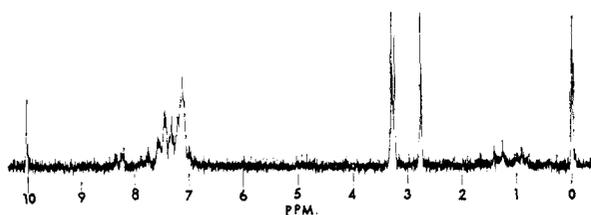


Fig. 1c.—Nuclear magnetic resonance spectrum of tris(methylphenylacetylene)tungsten carbonyl $(C_6H_5C\equiv CCH_3)_3W(CO)$.

spectrometer. The samples were examined in dilute solutions (5–10 wt.%) in acetone- d_6 and the hexyne complex I also in $CDCl_3$. Tetramethylsilane (TMS) was used throughout as the internal reference. Radiofrequency was held well below saturation intensity and a sweep rate of approximately 1.0 c.p.s./sec. was employed. The sample temperature was $25.0 \pm 0.5^\circ$ in all cases, and the hexyne complexes were handled under dry N_2 to minimize decomposition. The spectra were calibrated by the usual side-band technique, and line positions were reproducible to ± 0.01 p.p.m. or better.

Infrared Spectra.—The infrared spectra were recorded using a Perkin-Elmer 221 spectrophotometer equipped with a NaCl prism-grating interchange. The samples were examined as halocarbon oil and Nujol mulls from 3950 to 650 cm^{-1} , and in solution (CCl_4 , *n*-hexane) between 2100 and 1600 cm^{-1} . The spectra in solution were recorded with an expanded abscissa (12.5 $cm^{-1}/cm.$) and were calibrated with respect to the 1847.8 cm^{-1} band of atmospheric water vapor. Accuracy is ± 1 cm^{-1} with calibration and ± 3 cm^{-1} without calibration. Spectra of the mulls appear in Fig. 2; bands due to the medium are cross-hatched. Bands of the solution spectra are listed in Table I.

TABLE I

INFRARED ABSORPTIONS OF $(RC\equiv CR')_3W(CO)$ COMPLEXES^a

Compound/ medium	ν_{CO}	ν_{RCO}	$\Delta\nu$, obsd.	$\nu_{C\equiv C}$
I/ <i>n</i> -hexane	2034.3	1987.5	46.8	1702
II/ CCl_4	2071.8	2022.3	49.5	1680
III/ CCl_4	2057.0	2008.3	48.7	1731

^a In cm^{-1} .

Results and Discussion

Tris(hexyne)tungsten(0) monocarbonyl $(C_2H_5C\equiv CC_2H_5)_3W(CO)$ (I) was prepared by heating excess 3-

hexyne with either mono(acetonitrile)tungsten pentacarbonyl or tris(acetonitrile)tungsten tricarbonyl.³¹ Other disubstituted alkynes give analogous products. Thus, diphenylacetylene and methylphenylacetylene formed the stable complexes $(C_6H_5C\equiv CC_6H_5)_3W(CO)$ (II) and $(C_6H_5C\equiv CCH_3)_3W(CO)$ (III), respectively.

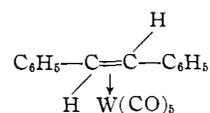
The 3-hexyne may be displaced and recovered by treatment of I with CO at 90° and 3000 p.s.i. Methylphenylacetylene may be recovered on a cold finger by vacuum pyrolysis of III.

Alkynes that contain a terminal hydrogen tended to cause decomposition and polymerization and no stable organometallic compounds were isolated. Acetylene, 1-hexyne, and phenylacetylene are examples of alkynes that gave brown polymeric residues in this reaction.

In attempting to extend this reaction to derivatives of chromium and molybdenum, completely different results were obtained under comparable reaction conditions. Reaction of 3-hexyne with $(CH_3CN)_3Mo(CO)_3$ did not appear to give a compound corresponding to the tungsten acetylenic complex. Hexaethylbenzene isolated from the reaction mixture indicates that the molybdenum complex causes cyclotrimerization of the acetylenic molecule.

The reaction of the chromium analog was complicated. Reaction of diphenylacetylene with $(CH_3CN)_3Cr(CO)_3$ gave a mixture of products. Thin layer chromatography showed a major component which was yellow but soon turned violet upon exposure to air. A chromatogram in the second dimension showed it to have an R_f value identical with authentic tetraphenylcyclopentadienone. Apparently an air-sensitive cyclopentadienone-chromium complex is formed by cyclodimerization of the diphenylacetylene with inclusion of a carbonyl group. This is consistent with results reported by others.^{5-8,32}

Whereas disubstituted acetylenes form complexes of the type I, reaction of stilbene and $(CH_3CN)W(CO)_5$ gave a rather normal exchange reaction to give an olefin complex



Acetylenes are known to undergo a wide variety of cyclizations, polymerizations, and rearrangements and, furthermore, may lead to di- and even trinuclear metal complexes on reaction with metal carbonyl compounds. In contrast, the chemical and physical properties of the compounds reported here suggest a rather straightforward structure, as discussed below.

The elemental analyses of I, II, and III show a complete lack of nitrogen indicating that all the starting nitrile groups were displaced. The molecular weights indicate a single mononuclear species. When the acetylene complexes are refluxed in ethanolic I_2 solution, only 1 molar equiv. of CO is evolved. Furthermore, spectroscopic examination of the residues after carbonyl determination gives no evidence of carbonyl groups, either organic or inorganic. From this, one may conclude that a single carbonyl group exists in the molecule.

The n.m.r. spectrum of I, shown in Fig. 1a, is rather dramatic and definitive. 3-Hexyne displays a typical

A_2B_3 type spectrum with the methylene group appearing as a quartet and the methyl group as a triplet at 2.30 and 1.24 p.p.m. below tetramethylsilane (TMS), respectively. Some fine structure is seen in the methylene resonance as expected and is due to long-range coupling through the triple bond. In contrast, the spectrum of I displays two quartets having equal intensity appearing at 3.54 and 3.07 p.p.m. below TMS and two triplets (overlapping) having equal intensity appearing at 1.34 and 1.09 p.p.m. below TMS. Also, there is no evidence for nonequivalence of protons within a methylene or methyl group. This suggests that all three acetylenic molecules are equivalent but that in each of the ligands one of the two ethyl groups is in a different environment from the other. Thus, we can conclude that the three ligand molecules in I are symmetrically arranged around the metal atom with three ethyl groups in the vicinity of the CO. The resonance lines of these CH_2 and CH_3 groups would be expected to appear at lower field than those arising from the ethyl groups extending in the opposite direction. Assuming that the above representation of the complex is correct, one would expect the methyl group in the vicinity of the CO to be less deshielded than its neighboring methylene. The lack of any observed long-range coupling in the methylene group indicates that the triple bond is perturbed and represents strong evidence that the ligand is bonded to the metal *via* π -complexing through the triple bond. In addition, upon examining the proton n.m.r. region characteristic of metal hydrides³³ no evidence was found for the presence of such in I, II, or III.

The n.m.r. spectrum of II is shown in Fig. 1b and appears to be consistent with the results obtained on the hexyne complex. It is seen that there are three groups of resonance lines, each displaying complex line splitting. The lowest field group is believed to be due to the *ortho* protons which are in the vicinity of CO and the second group due to the *ortho* protons which are on the phenyl rings extending in the opposite direction of the CO. The highest field group arises from the *meta* and *para* protons of both types of phenyl groups. The relative areas under these groups are in the ratio of 2:2:6 which is a necessary requirement of the proposed structure. A detailed analysis of the line splittings may be carried out later. One is led to the conclusion that the bonding and stereochemistry in II are very similar to that in the hexyne complex.

The n.m.r. spectrum of III is shown in Fig. 1c and, in general, is consistent with those of I and II. This is the only compound in the series in which the ligand is not symmetrical about the triple bond, and therefore it is possible to have geometric isomers within the same basic structure. The methyl resonance line in pure methylphenylacetylene appears at 2.01 p.p.m. below TMS. It was observed with the hexyne that the resonance lines of the methylene groups in the environment of the CO are shifted downfield 1.24 p.p.m., and those of the ones extending in the opposite direction are shifted downfield 0.77 p.p.m. Assuming that approximately the same shifts are observed in this case, one would expect resonance lines for the methyl group to appear at approximately 2.78 and 3.25 p.p.m. Resonance lines are observed in these regions and this

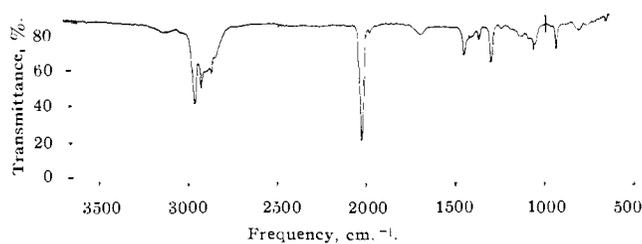


Fig. 2a.—Infrared spectrum of $(C_2H_5C\equiv CC_2H_5)_3W(CO)$; halocarbon oil, Nujol mull.

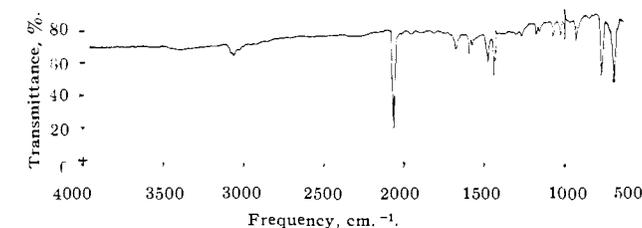


Fig. 2b.—Infrared spectrum of $(C_6H_5C\equiv CC_6H_5)_2W(CO)$; halocarbon oil, Nujol mull.

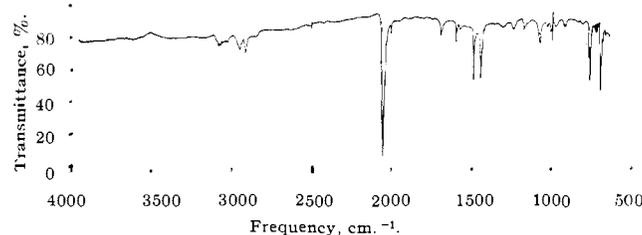


Fig. 2c.—Infrared spectrum of $(C_6H_5C\equiv CCH_3)W(CO)$; halocarbon oil, Nujol mull.

constitutes strong evidence that geometrical isomers are indeed present. The resonance lines in the aromatic ring region can largely be explained in the same manner. If one can determine which isomers are present, it would be possible to calculate the amount of each by utilizing the n.m.r. data.

The infrared spectra of the mulls of the complexes (I, II, III) are given in Fig. 2. They show one strong band for the A_1 metal carbonyl stretching mode assuming C_3 or C_{3v} symmetry. The high frequency of the band indicates that the single carbonyl group is terminal. A weak, sharp band on the low frequency side of the metal carbonyl band is assigned as the ^{13}CO mode. The band is of the expected intensity^{34a} considering the natural abundance of this isotope. Also, identical solid-state splitting is observed for this band and the main carbonyl band in the spectra of mulls of II, which certainly suggests a close relationship between the carbonyl stretching and the vibration that gives rise to the weak band. A possible alternative assignment of the band as due to metal-hydrogen stretch is remote as noted from the n.m.r. evidence (see above) and the synthesis of the complexes in the complete absence of materials with active hydrogen.

The isotopic shift for the stretching frequency of the unique CO group (see Table I) is much larger than usually found for the isotope shift in other metal carbonyls.³⁴ No measurements have yet been reported

(34) (a) S. L. Shufler, H. W. Sternberg, and R. A. Friedel, *J. Am. Chem. Soc.*, **78**, 2687 (1956); (b) R. A. Friedel, I. Wender, S. L. Shufler, and H. W. Sternberg, *ibid.*, **77**, 3951 (1955); (c) B. L. Ross, J. G. Grasselli, W. M. Ritchey, and H. D. Kaesz, *Inorg. Chem.*, **2**, 1023 (1963).

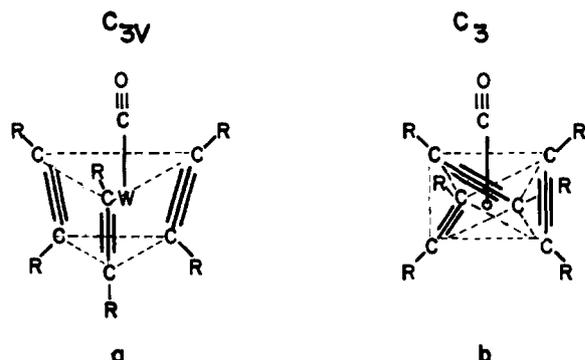


Fig. 3.—Proposed tetrahedral and distorted octahedral configurations for $(RC\equiv CR')W(CO)$.

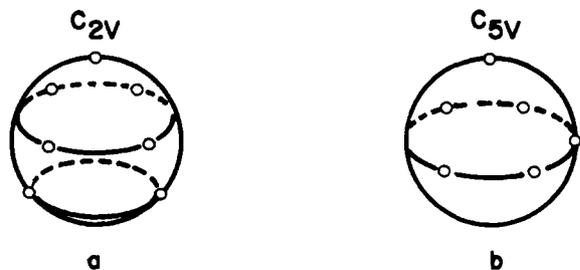


Fig. 4.—Alternative seven-coordinate structures.

for complexes containing a single metal carbonyl group although such compounds are known.³⁵ In I, II, and III there is a unique CO group much like the unique NO group in $Co(CO)_3(NO)$.³⁶ In the latter, the observed frequencies for ^{14}NO and ^{15}NO yield a shift of 36 cm^{-1} , which is greater than that given by the calculation $\nu^{15}NO = \nu^{14}NO[14(15 + 16)/15(14 + 16)]^{1/2}$, which would be 33 cm^{-1} for $\nu^{14}NO$ at 1822 cm^{-1} . After corrections for anharmonicity, the observed frequencies³⁶ yield a shift of 33 cm^{-1} , while the shift for frequencies calculated by normal coordinate analysis is a little higher, 38 cm^{-1} . This leads to a more reasonable comparison between expected and observed shifts. In the complexes presently under consideration, the observed (uncorrected) carbonyl frequencies also yield shifts (Table I) which are generally a little higher than the shift calculated from the simplified relationship, $\nu^{13}CO = \nu^{12}CO[12(13 + 16)/13(12 + 16)]^{1/2}$. No doubt a normal coordinate analysis will give frequencies whose shifts are slightly higher than our observed values. A comparison of the frequencies from normal coordinate treatments and the force constants for the carbonyl in these complexes with results for complexes containing more than one carbonyl group would be most interesting.

A broad, weak band in the region of 1700 cm^{-1} (Table I) is assigned to the coordinated $C\equiv C$ stretching vibration. The shift of over 400 cm^{-1} from the usual position for this vibration indicates that coordination to the metal is of a doubly π -bonded nature as in $Pt(R_3P)_2ac^{23}$ and $ReCl(ac)_2$,²⁴ in contrast to bonding noted for acetylene $Pt(II)$ complexes.³⁷ In the latter complexes, the $C\equiv C$ stretching vibrations, similar to the

(35) (a) W. Hieber and E. Bockly, *Z. anorg. allgem. Chem.*, **269**, 308 (1952); (b) R. D. Cowan, *J. Chem. Phys.*, **18**, 1101 (1950); (c) E. O. Fischer, H. P. Kögler, and P. Kuzel, *Ber.*, **93**, 3006 (1960); (d) C. G. Barclough and J. Lewis, *J. Chem. Soc.*, 4842 (1960).

(36) R. S. McDowell, W. D. Horrocks, and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

(37) J. Chatt, I. A. Duncanson, and R. G. Guy, *Chem. Ind. (London)*, 430 (1959).

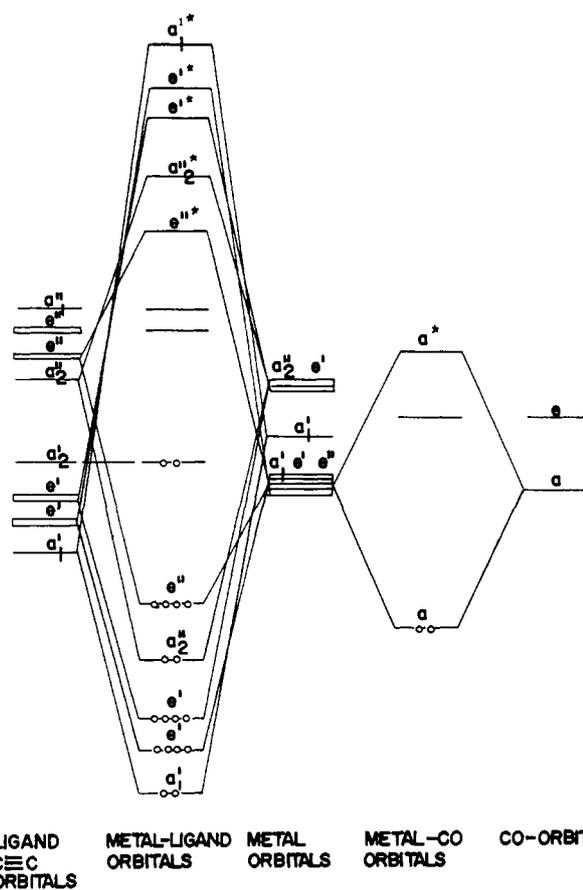


Fig. 5.—Energy level diagram for $(RC\equiv CR')_3W(CO)$, C_{3v} .

$C\equiv C$ stretching vibration of olefin π -complexes, is lowered by 150 cm^{-1} .

Except for small shifts in position and slight changes in relative intensity, the ligand vibrations are essentially those of the free ligands. This striking similarity excludes the possibility of cyclization of the ligands with the inclusion of carbon monoxide as noted for a number of metal complexes of acetylenes.⁸⁻¹⁴ The alternate possibility of cyclization of the ligands to the hexa-substituted benzenes can also be excluded since the C-C stretching bands of the π -complexed aromatic ring³⁸ do not appear in the spectra.

Based on the evidence cited above, there are two structures that seem most probable (Fig. 3). Figure 3a shows a structure with C_{3v} symmetry where the ligands may be considered arranged pseudo-tetrahedrally (to the center of the triple bond). This allows the symmetrical placing of the alkynes and the different environment of one end of the alkyne by proximity to the carbonyl. By twisting the alkynes out of the plane of the metal-CO bond and considering the complex as a type of seven-coordination, one gets a C_3 symmetry that is also consistent with the n.m.r. evidence (Fig. 3b). Other seven-coordinate structures (Fig. 4) are not compatible with the n.m.r. data. The type of seven-coordination shown in Fig. 3b would be a very distorted octahedron with the CO extending from a face of the octahedron.

There is little to be gained, however, by considering a distorted octahedron because the triple bond distance of an alkyne is by far too short to fit along the edge of a regular octahedron. The structure must become so

(38) R. E. Humphrey, *Spectrochim. Acta*, **17**, 93 (1961).

distorted as to be unsatisfying as a seven-coordinate system. A tetracoordinate picture is probably more realistic and will be used for the molecular orbital treatment below.

The effective atomic number (EAN) for tungsten requires that only ten electrons should be donated by the acetylenic ligands. This means two of the acetylenic ligands donate both their π -electron pairs (similar to $\text{Pt}(\text{R}_3\text{P})_2\text{ac}^{23}$ and $\text{ReCl}(\text{ac})_2^{24}$) and the third only one. Since proton magnetic resonance, however, indicates that all acetylene ligands are bonded equivalently, we have to assume that the lone electron pair is resonated through the entire carbon system.

A qualitative MO scheme derived from overlap of appropriate AO's of the metal with the ligands is given in Fig. 5. The two excess electrons may occupy a lone pair a_2 ligand MO which nicely explains the diamagnetism of this complex.

If we consider structure b in Fig. 3 with a C_3 symmetry, the simple Hückel MO treatment does not change the qualitative picture. The ligand π -orbital system may be overlapped in the same way with the metal AO's as shown. In this case also, the excess pair of electrons enters a nonbonding a -orbital. Since the acetylene ligands are twisted to the C_3 axis and the π -orbitals of the $\text{C}\equiv\text{C}$ bond also have to be twisted to each other to give a reasonable overlap with the metal

AO's, a more accurate treatment becomes rather cumbersome.

Conclusions

Tris(hexyne)tungsten(0) monocarbonyl, tris(diphenylacetylene)tungsten(0) monocarbonyl, and tris(methylphenylacetylene)tungsten(0) monocarbonyl constitute a unique new group of complexes of tungsten. The structures of all three are similar, with the ligands arranged symmetrically around the metal and doubly π -complexed through the $\text{C}\equiv\text{C}$. The presence of only one CO is confirmed by chemical and spectroscopic evidence. Similar complexes are not obtained with Cr or Mo or with terminal alkynes. Although the electronic picture for these complexes is most unusual, in that there are two more electrons than necessary for tungsten's EAN, a simple MO treatment shows that the electron pair can be accommodated in a suitable nonbonding orbital in either a C_{3v} or C_3 symmetry. Further confirmation of structure must await an X-ray crystallographic analysis which is currently underway.³⁹

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(39) L. F. Dahl, University of Wisconsin, Madison, Wis.

[CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY, UNIVERSITY OF MUNICH, GERMANY]

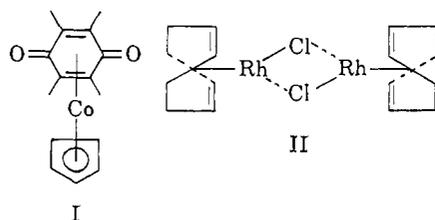
Preparation and Properties of Some Duroquinone π -Complexes of Cobalt, Rhodium, and Iridium^{1,2}

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The reduction of rhodium and iridium trichlorides with ethanol in the presence of duroquinone yields duroquinone π -complexes of rhodium(I) and iridium(I) chlorides, respectively. Reaction with cyclopentadienylrhodium produces the very stable duroquinonecyclopentadienylmetal compounds, which are compared with the previously prepared cobalt complex. The electronic spectra of these complexes are discussed, and the observed transitions are calculated on a semiempirical basis, using simple MO theory. From the infrared spectra of the complexes, it is concluded that the π -bonded duroquinone molecule must be nonplanar, and an explanation for this effect is given.

Recently, the electronic spectra of a number of quinone π -complexes of nickel were successfully interpreted on the basis of a molecular orbital treatment.⁴ This



work is now being extended to complexes of other transition metals. It was reported a short time ago² that dicarbonylcyclopentadienylcobalt reacts with duroqui-

none to produce a duroquinone complex of cobalt, $\text{DquCoC}_5\text{H}_5$ (I). In view of its remarkable stability and its well-resolved electronic spectrum, it appeared to be of interest to prepare the analogous complexes of rhodium and iridium.

Results

Duroquinone π -Complexes of Rhodium.—The Rh(I) valence state may be stabilized with chelating dienes. If rhodium trichloride is reduced with hot ethanol in the presence of, *e.g.*, 1,5-cyclooctadiene, the dimeric cyclooctadienechlororhodium(I), compound II, is obtained.^{5,6} We have made use of this reaction to prepare duroquinone π -complexes of rhodium(I) chloride. Refluxing solutions of duroquinone and $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ in ethanol for 3 hr. yields, in addition to small amounts of a soluble complex, an insoluble orange product which roughly analyzes for $(\text{DquRhCl})_x$. This complex (III) is probably a halogen-bridged coordination polymer. It reacts with pyridine to produce a red bispyridine adduct (IV)

(1) Paper VIII on Quinone π -Complexes of Transition Metals; presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

(2) Paper VII: G. N. Schrauzer and H. Thyret, *Angew. Chem.*, **75**, 641 (1963).

(3) Visiting Fellow, 1962–1963, Shell Development Company, Emeryville, Calif.

(4) G. N. Schrauzer and H. Thyret, *Theoret. Chim. Acta*, **1**, 172 (1963).

(5) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

(6) G. Wilkinson, M. A. Bennett, and E. W. Abel, *ibid.*, 3178 (1959).