1975

Zwitterionic Carbonyl Halide Complexes of Tungsten

Dragoslav Marcovich

Eastern Illinois University

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ZWITTERIONIC CARBONYL HALIDE

COMPLEXES OF TUNGSTEN

(TITLE)

BY

DRAGOSLAV MARCOVICH
BACHELOR OF SCIENCE
UNIVERSITY OF ILLINOIS
URBANA ILLINOIS
AUGUST 1973

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF

Master of Science in Chemistry

IN THE GRADUATE SCHOOL, EASTERN ILLINOIS UNIVERSITY
CHARLESTON, ILLINOIS

1975

YEAR

I HEREBY RECOMMEND THIS THESIS BE ACCEPTED AS FULFILLING
THIS PART OF THE GRADUATE DEGREE CITED ABOVE

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BY

DRAGOSLAV MARCOVICH
BACHELOR OF SCIENCE
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ZWITTERIONIC CARBONYL HALIDE COMPLEXES OF TUNGSTEN

Thesis approved

Dr. R.L. Keiter, Thesis Advisor

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ABSTRACT

Title of Thesis: Zwitterionic Carbonyl Halide Complexes
of Tungsten

Dragoslav Marcovich, Master of Science, 1975

Thesis directed by: Dr. Richard L. Keiter

The first carbonyl halide zwitterionic complexes have been synthesized and are of the type cis-
 $(OC)_4XWPPh_2(CH_2)_n^+PPh_2R$ in which X is Cl, Br, or I, n is 1 or 2, and R is an alkyl group. The complexes were prepared by the reaction

The temperature of the reaction must be carefully controlled since the decomposition point of the product is only 10°C higher than that of the reactant.

The zwitterionic complexes are sensitive to light in solution but are insensitive to light in the solid state. Unlike carbonyl halide complexes of the type $(R_4N)(XW(CO)_5)$, the zwitterionic complexes are not as sensitive.

*If you stop every time a dog barks,
your road will never end.*

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The zwitterionic complexes were characterized by infrared, ultraviolet/visible and proton NMR spectroscopy and by elemental analyses.

INTRODUCTION

The formation of zerovalent carbonyl halide zwitterions was postulated, but not confirmed, by D. P. Shah in 1971 during his work on tungsten carbonyl complexes with positively charged phosphorus ligands.¹ One of the complexes used in Shah's study was a 1:1 electrolyte of the type $\text{W(CO)}_5\text{PPh}_2\text{P}^+(\text{CH}_2)_2\text{P}^-\text{Ph}_2\text{R X}$ in which X is a halogen and R is an alkyl group. This complex was prepared by one of two methods, both of which utilized anilinepentacarbonyl-tungsten(0), $(\text{OC})_5\text{WNH}_2\text{Ph}$, as a starting material.² The two reaction sequences are shown with the following equations:

In the latter reaction, in addition to recovering some of the desired 1:1 electrolyte, a rather insoluble side product was isolated which was thought to consist primarily of a carbonyl halide zwitterion of the type:

The postulation of this new class of carbonyl halides was based solely upon infrared analysis of the carbonyl region. The carbonyl region of the infrared spectrum consisted of five bands occurring at 2071, 1982, 1932, 1902 and 1834 cm^{-1} . The band at 1982 was attributed to tungstenhexacarbonyl, a common contaminant in this type of reaction. If the other four bands belonged to one complex it was reasonable to postulate a cis structure since cis- $\text{L}_2\text{W}(\text{CO})_4$ complexes are known to give rise to four CO bands. The trans- $\text{L}_2\text{W}(\text{CO})_4$ isomers give rise to only one CO band.³

Shah ruled out the possibility of a disubstituted complex such as cis- $\text{W}(\text{CO})_4(\text{Ph}_2\text{PCH}_2\text{PPh}_2\text{CH}_3)_2$ because one of the observed carbonyl stretching frequencies (1834 cm^{-1}) was too low to be assigned to a cis complex if both coordination sites are occupied by phosphorus. For example, in the complex cis-($\text{C}_4\text{H}_9\text{Ph}_2\text{P}$) $_2\text{W}(\text{CO})_4$ the carbonyl stretching frequencies are at 2018, 1918, 1898, and 1890 cm^{-1} . The very low stretching frequency at 1834 cm^{-1} was thought to be reasonable if a halogen were attached to tungsten. Unfortunately the side product which gave rise to the infrared spectrum

was not purified and the existence of the zwitterion was not confirmed. It has been the purpose of this work to systematically develop a synthetic route for the preparation of a novel class of zwitterionic complexes and to characterize their physical properties.

Zwitterions of organic nature are abundant and naturally occurring. Every amino acid, $\text{H}_3\text{N}^+\text{R}\text{COO}^-$, at its isoelectric point is a zwitterion, and in this category are also betaines such as the betaine of glycine, $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{COO}^-$. Inorganic zwitterions have been investigated only in recent years. In 1962 Quagliano and coworkers complexed the betaine of glycine to Co(II) , Ni(II) and Cu(II) to obtain the first zwitterionic complexes.⁴ These pseudotetrahedral complexes were of the type:

This team of workers continued to pursue the investigation of zwitterionic complexes and in their next report on this subject synthesized and characterized complexes of aminoethyltrimethylammonium cations with Co(II) , Ni(II) , Cu(II) , Zn(II) and Cd(II) . Both tetrahedral and octahedral complexes were formed.

From their spectral work it was concluded that the presence

of a positive charge on the ligand does not hinder the formation of transition metal complexes.⁵

Since this pioneer work Bergelund and Meek prepared 3-[(diphenylphosphino)methyl]-3-methyl-1,1-diphenylphosphatonium metal halides

the first zwitterionic complex containing a phosphorus ligand.⁶

In 1969 Quagliano's group prepared metal halide diphosphino zwitterions of the general formula⁷

In the same year Dahlhoff used the ligand shown below to prepare metal halide zwitterions of the type MX_3L^- .⁸

In 1973 Taylor and Kolodny reported a metal halide zwitterionic complex of Co(II) containing the ligand $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{NR}_2^+\text{HX}^-$.⁹

A rather novel zwitterion was prepared by Rico and Longato who used a cobalt complex, $\left[\text{Co}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2(\text{CN})_2\right]^+$, as a ligand, allowing it to react with metal (II) halides.¹⁰

For example:

All of the inorganic zwitterions cited above have been prepared in the same general way, i.e., from the reaction of a metal salt and a monoquaternized ligand. In each case the metal is in the +2 oxidation state, and the complexes tend to be insoluble in organic solvents. Most are only sparingly soluble in water.

Since zwitterionic carbonyl halide complexes of tungsten are of principal interest in this study it is worthwhile to review briefly the carbonyl halide chemistry of tungsten.

Carbonyl halides of tungsten have been known since 1966 when Colton and Tomkins reported that $\text{W}(\text{CO})_4\text{Cl}_2$ could be prepared from $\text{W}(\text{CO})_6$, and liquid chlorine. The bromo

and iodo complexes were isolated by the same workers several years later by the application of analogous reactions.¹¹⁻¹³

Carbonyl halide complexes of tungsten containing phosphines have been synthesized by two routes:

These seven-coordinate complexes obey the effective atomic number rule. Since tungsten is in the +2 oxidation state the addition of fourteen dative electrons, supplied by seven ligands, gives the required thirty-six electron configurations of the noble gas Argon. These complexes are of interest in this thesis because they are the only known examples of complexes of tungsten which contain carbonyls, halides and phosphines as ligands.¹⁴

Carbonyl halides of zerovalent tungsten are also known and can be prepared by refluxing a halide salt with tungsten hexacarbonyl in diglyme:

If alkali metal halides are used, the resulting complexes are too unstable to isolate.¹⁵ When the cation is a tetraalkylammonium ion the complexes are stable enough to isolate, but decompose if placed in air for a few minutes. Apparently larger cations stabilize the lattices containing larger anions more effectively than small cations. As pointed out earlier in the discussion, the metals of all

previously prepared zwitterions are in the +2 oxidation state.

The purpose of this work was to find a synthetic route by which one could prepare zwitterions in which the metal is in the zero oxidation state and to investigate the properties of the complexes. These complexes were chosen to be prepared:

CHAPTER II

RESULTS AND DISCUSSION

A number of different approaches were used to synthesize the zwitterions. The following reactions in which $n = 1$ or 2 and $R = \text{alkyl}$ represent those approaches.

(3)

followed by

The reaction sequences (1) and (2) above were tried in the beginning stages of this research but the mixture which resulted was difficult to separate and at that time the light sensitivity of a zwitterion of the type $X(OC)_4^- W PPh_2(CH_2)_n^+ PPh_2R$ had not yet been discovered. Since no precautions were used to protect solutions of products from light it is not surprising that pure product was not obtained from those reactions at that time. The successful synthesis of the zwitterion was first achieved with reaction 3b.

The first step in the sequence of reactions used in this work was to prepare the monoquaternized diphosphine salts. Quagliano⁷ prepared benzyl derivatives of $PPh_2CH_2PPh_2$ and $PPh_2(CH_2)_2PPh_2$ by the direct reaction of $PhCH_2Br$ and the phosphine in benzene solution.

The benzyl salt, however, is not very soluble and for that reason quaternized salts of CH_3I , C_2H_5Br , and C_3H_7Cl were prepared.

The reaction of CH_3I with $PPh_2CH_2PPh_2$ was straightforward. When the two reactants are mixed in 1:1 stoichiometric ratios at room temperature $PPh_2CH_2^+ PPh_2CH_3 I^-$ slowly precipitates from the solution.

NMR spectroscopy was used to establish the identity of the product. The NMR spectrum of the starting material, $\text{PPh}_2\text{CH}_2\text{PPh}_2$, is shown in Figure 1. The two equivalent phosphorus-31 nuclei, which have a spin of $\frac{1}{2}$, split the protons into a triplet ($J_{\text{P-H}} = 1.3 \text{ Hz}$) which occurs at 2.80 ppm. The product, $\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ I}^-$, gives rise to a doublet ($J_{\text{P}^+\text{-CH}_2} = 15.6 \text{ Hz}$) at 4.20 ppm shown in Figure 2. The coupling, $J_{\text{P-CH}_2}$, is too small to be resolved, a doublet ($J_{\text{P}^+\text{-CH}_3} = 13.5 \text{ Hz}$) was found at 2.71 ppm.

Similarly the phosphonium salt, $\text{Ph}_2\text{P}^+(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ I}^-$, was isolated. There were difficulties encountered, however, in this preparation as there was a tendency for the di-quaternized salt, $\text{CH}_3\text{P}^+\text{Ph}_2(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ 2I}^-$, to form. Apparently the greater solubility of $\text{PPh}_2(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ I}^-$ over $\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ I}^-$, the steric requirements of $\text{CH}_3\text{P}^+\text{Ph}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3 \text{ 2I}^-$, and the charge separation explain why the synthetic difficulty was encountered only with the ethane derivative. The insolubility of the diquaternized salt did not allow an NMR spectrum to be obtained. The NMR spectrum of 1,2-bis(diphenylphosphino)ethane is shown in Figure 3. It is seen to contain an apparent triplet ($J_{\text{P-H}} = 4.0 \text{ Hz}$) at 2.10 ppm. The NMR spectrum of the mono-quaternized product, 1-diphenylphosphino,2-methyldiphenylphosphonium-ethane iodide, is shown in Figure 4. The doublet ($J_{\text{P}^+\text{-CH}_3} = 14.0 \text{ Hz}$) at 2.91 ppm falls in the complex methylene pattern.

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF 1,2-BIS(DIPHENYLPHINO)METHANE

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF $(\text{C}_6\text{H}_5)_2\text{P}(\text{OC}_6\text{H}_5)_2\text{I}^-$ + DIPHENYLPHOSPHINOMETHYLDIPHENYLPHOSPHONIUMMETHANE IODIDE

The quaternization of 1,1-bis(diphenylphosphino)-methane with $\text{C}_2\text{H}_5\text{Br}$ did not proceed nearly as rapidly as did the reaction with CH_3I . Excess $\text{C}_2\text{H}_5\text{Br}$ was used and the reaction mixture had to be refluxed in benzene for 6 hours. Figure 5 shows the NMR spectrum of $\text{PPh}_2\text{CH}_2^+\text{PPh}_2\text{C}_2\text{H}_5 \text{Br}^-$. A doublet ($J_{\text{P}^+\text{CH}_2} = 14.8 \text{ Hz}$) occurs at 4.20 ppm. The $J_{\text{P}-\text{CH}_2}$ is too small to be resolved. The methyl group of $-\text{C}_2\text{H}_5$ is found at 1.10 ppm. It is split by P-31 ($J_{\text{P}^+\text{C}-\text{CH}_3} = 21.0 \text{ Hz}$) and by the methylene protons ($J_{\text{CH}_2-\text{CH}_3} = 7.4 \text{ Hz}$). The complex methylene falls at 3.20 ppm.

The quaternization of $\text{PPh}_2\text{CH}_2\text{PPh}_2$ with $\text{C}_3\text{H}_7\text{Cl}$ took even longer than with $\text{C}_2\text{H}_5\text{Br}$, requiring 10 hours at reflux temperature. The salt, though never fully purified, gave characterizable products in subsequent reactions.

The next step in the synthesis of the zwitterions was to coordinate the ligands, 1-diphenylphosphino,1-methyldiphenylphosphonium-methane iodide, 1-diphenylphosphino, 2-methyldiphenylphosphonium-ethane iodide, 1-diphenylphosphino,1-ethyldiphenylphosphonium-methane bromide, 1-diphenylphosphino,1-propyldiphenylphosphonium-methane chloride to tungsten. If one uses the usual methods of photolyzing or thermally decomposing W(CO)_6 in the presence of the ligand, a mixture of cis, trans, and monosubstituted products are usually obtained.¹⁶ Initially, to eliminate the formation of a mixture of products the reactions used previously by Shah were utilized.¹ These reactions require $\text{PhNH}_2\text{W(CO)}_5$ to be prepared from PhNH_2 and W(CO)_6 .

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF DIPHENYLPHOSPHONIUMMETHYLPHENYLPHOSPHONIUMETHANE IODIDE
 $(C_6H_5)_2PCH_2P(C_6H_5)_2CH_3 \quad I^-$

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF DIPHENYLPHOSPHINOETHYLDIPHENYLPHOSPHONIUM METHANE BROMIDE
 $(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}^+(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_3 \text{ Br}^-$

Yields are not very good for this reaction and the aniline complex is unstable in solution. When put in solution with a phosphine ligand the following reaction proceeds in good yield.

In order to eliminate one of the steps of the two step preparation, a modified photolysis reaction recently reported by Taylor, et al. was utilized.⁹ If W(CO)_6 is irradiated for several hours in THF prior to the addition of the phosphine ligand the following reaction takes place.

When the phosphine ligand is added to the solution of the unstable THF complex the desired 1:1 electrolyte is obtained.

The above procedure eliminates the preparation, isolation, and purification of an intermediate complex and also allows better yields of the 1:1 electrolyte to be obtained. Thus the following 1:1 electrolytes were prepared with the reactions given above.

The proton NMR spectrum (Figure 6) of $(OC)_5WPPh_2CH_2^+PPh_2CH_3^-$ I confirms the structure of the complex. The methylene resonance appears as a doublet of doublets ($J_{WP-CH_2} = 7.5$ Hz; $J_{P^+-CH_2} = 16.0$ Hz) centered at 4.42 ppm. In addition the methyl group appears as a doublet ($J_{P^+-CH_3} = 13.5$ Hz) at 2.25 ppm.

The proton NMR spectrum (Figure 7) of $(OC)_5WPPh_2(CH_2)_2^+PPh_2CH_3^-$ I shows the expected doublet ($J_{P^+-CH_3} = 14.0$ Hz) at 3.05 ppm while the complicated methylene absorption is found between 2 and 3 ppm.

The complex, $(OC)_5WPPh_2CH_2^+PPh_2C_2H_5^-$ Br, was never made analytically pure. Purification of these types of complexes has been shown to be difficult in the past. Often these salts are converted to PF_6^- salts which are more easily recrystallized than the halide salts.¹ For this work such a conversion from halide to PF_6^- , would not be meaningful since the halide ion is needed in the complex for the formation of the zwitterion. An NMR spectrum of the impure complex is shown in Figure 8.

Carbonyl stretching frequencies for the 1:1 electrolytes are shown in Table I and infrared spectra for these complexes are shown in Figures 9, 10, and 11. These spectra are characteristic of carbonyl complexes, $W(CO)_5$, of C_{4v} symmetry and fully support the assigned structures. Carbonyl stretching frequencies are highly dependent upon the electronegativity of the substituents attached to the phosphorus ligand. Since all of these ligands are very similar it is

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF $\text{W}(\text{CO})_5(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2\text{I}^-$ DI-PHENYL-PHOSPHINO-METHYL-DI-PHENYL-PHOSPHONIUM-METHANE-PENTACARBONYL-TUNGSTEN(0) IODIDE

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF DIETHYLPHOSPHINOETHYL DIPHENYLPHOSPHINE OXIDE (O) IODIDE
 $\text{H}(\text{CO})_2(\text{C}_6\text{H}_5)_2\text{P}(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_3$

not surprising that the infrared spectra are also very similar.¹⁷

The conversion of a $(OC)_5WPPh_2CH_2^+PPh_2R^- \bar{X}$ complex into a zwitterion is best accomplished by heating the 1:1 electrolyte in diglyme at just above its decomposition point.¹⁸ The complex, cis- $(OC)_5WPPh_2CH_2^+PPh_2CH_3^- \bar{I}$, decomposes at 160°C.

If the reaction is allowed to continue for longer than about 15 minutes or if the temperature of the reaction rises above 170°C decomposition takes place. It is thus good fortune that the narrow range of conditions were found and that the product is more stable than the reactant. The conversion of $(OC)_5WPPh_2CH_2^+PPh_2CH_3^- \bar{I}$ into the zwitterion is demonstrated dramatically in Figure 10 which shows the infrared spectra of the starting material and product. A trans complex would be expected to give rise to only one CO stretching frequency. Statistically there is only a 20% chance trans would form.

TABLE I

Carbonyl Infrared Stretching Frequencies for the 1:1 Electrolytes (cm⁻¹)

$W(CO)_5PPh_2CH_2^+PPh_2CH_3^- \bar{I}$	2078	1989	1938
$W(CO)_5PPh_2(CH_2)_2^+PPh_2CH_3^- \bar{I}$	2080	1995	1939
$W(CO)_5PPh_2CH_2^+PPh_2C_2H_5^- Br$	2079	1991	1941

NUCLEAR MAGNETIC RESONANCE SPECTRUM OF DIPHENYLPHOSPHINOETHYLDIPHENYLPHOSPHONIUMMETHANEPENTACARBONYLTUNGSTEN(0) BROMIDE
 $\text{W(CO)}_5(\text{C}_6\text{H}_5)_2\text{PCH}_2\text{P}^+(\text{C}_6\text{H}_5)_2\text{CH}_2\text{CH}_3 \text{ Br}^-$

CARBONYL INFRARED STRETCHING SPECTRUM OF $\text{H(CO)}_5(\text{C}_6\text{H}_5)_2\text{P}^+(\text{C}_6\text{H}_5)_2\text{Cl}_2\text{Cl}_3 \text{ Br}^-$
IN DICHLOROMETHANE

CARBONYL INFRARED STRETCHING SPECTRA OF

In a similar fashion $(OC)_5WPPh_2(CH_2)_2P^+Ph_2CH_3 I^-$ can be converted into its zwitterion and that conversion is seen in the infrared spectrum shown in Figure 11.

The proton NMR spectrum of $I(OC)_4W^+PPh_2CH_2P^+Ph_2CH_3$ is shown in Figure 12. In addition to the complex phenyl absorption the spectrum consists of a doublet of doublets ($J_{WP-CH_2} = 5.6$ Hz; $J_{P^+-CH_2} = 16.4$ Hz) at 4.58 ppm and a doublet ($J_{P^+-CH_3} = 14.0$ Hz) at 2.78 ppm.

The $Br(OC)_4W^+PPh_2CH_2P^+Ph_2C_2H_5$ zwitterion was prepared in an analogous fashion to the above mentioned zwitterions and its infrared spectrum is shown in Figure 13.

The preparation of the chloro zwitterion was unexpected. From the reaction of $PPh_2CH_2P^+Ph_2C_3H_7 I^-$ and $W(CO)_5THF$, $Cl(OC)_4W^+PPh_2CH_2P^+Ph_2C_3H_7$ was isolated directly. Support for this conclusion comes from the infrared spectrum (Figure 14) which is quite similar to the spectra for the bromo and iodo complexes. The overall reaction can be represented as

It is unclear at this point whether the reaction conditions for the formation of the chloro zwitterion were different from those for the bromo and iodo complexes. Further work on this reaction is necessary.

FIG 12

SPECTRUM OF

CARBONYL INFRARED STRETCHING

IN DICHLOROMETHANE

CARBONYL INFRARED STRETCHING SPECTRUM OF
BIS(BENZYL)PHOSPHINE

Preliminary work, based on infrared data (Figure 15), reveals that the zwitterions may also be prepared by the reaction

although the synthesis needs further investigation.

The infrared data for the carbonyl zwitterions is shown in Table II. It is at first glance disturbing that carbonyl stretching frequencies change so little in going from the chloro complex to the iodo complex since the Cl group is more electronegative than the I group.

A search of the literature, however, reveals that a similar trend has been found for salts of the type $[(R_4N)^+][W(CO)_5X]^-$ (Table III).¹⁹⁻²⁰ It appears that the invariance observed in the carbonyl stretching frequencies can be accounted for if one takes into account the fact that Cl^- is a better π donor than I^- but I^- is a better $d\pi$ acceptor than Cl^- . The net result is that about the same amount of electron density ends up on the metal from both halide ligands. The Br^- ligand is an intermediate π donor and $d\pi$ acceptor.

Complexes of $[(R_4N)^+][IW(CO)_5]^-$ are known to be oxygen sensitive.²⁰ The zwitterionic complexes of this study are insensitive to oxygen in both the solid state and in solution. The iodo zwitterionic complexes are quite sensitive to light in solution although they are insensitive in the solid state.

TABLE II

Carbonyl Infrared Stretching Frequencies for the Zwitterions

	(cm ⁻¹)			
$\text{IW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3$	2016	1914	1881	1828
$\text{IW}(\text{CO})_4\text{PPh}_2(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3$	2013	1899	1880	1821
$\text{BrW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{C}_2\text{H}_5$	2018	1907	1878	1824
$\text{ClW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{C}_3\text{H}_7$	2016	1903	1876	1821

TABLE III

Carbonyl Stretching Frequencies for $\text{M}(\text{CO})_5\text{X}$ Types (cm⁻¹)

$(\text{CO})_5\text{CrI}$	2045	1915	1856
$(\text{CO})_5\text{CrBr}$	2055	1921	1857
$(\text{CO})_5\text{CrCl}$	2058	1921	1856
$(\text{CO})_5\text{WI}$	2060	1917	1854
$(\text{CO})_5\text{WBr}$	2063	1915	1845
$(\text{CO})_5\text{WCl}$	2065	1913	1847

E. Abel and I. Butler, Trans. Farraday Soc. 63, 45 (1967)

CARBONYL INFRARED STRETCHING SPECTRA OF

AND

BOTH WERE PREPARED FROM THE NORBORNADIENETETRACARBONYLTUNGSTEN(0) COMPLEX

If a chloroform solution of cis-I(OC) $_4$ $\bar{W}$ PPh $_2$ CH $_2$ P $^+$ Ph $_2$ CH $_3$ is exposed to sunlight for several hours, the change in the carbonyl region of the infrared spectrum (Figure 16) reveals the decomposition of the complex. Similarly the UV-visible spectrum (Figure 17) changes. The decomposition products of the light reaction have not been characterized although the infrared spectrum which results suggests that a complex of C $_{4v}$ symmetry forms. As decomposition proceeds, a fine brownish precipitate was observed to appear although in quantities too small to be characterized. If one shields the zwitterionic solution from light and passes oxygen gas through the solution for 24 hr there is no change in either the UV-visible or infrared spectrum of the complex. It was also demonstrated that the zwitterionic complexes decompose when exposed to sunlight when oxygen is not present in solution. It is therefore apparent that the light sensitivity of the complexes is unrelated to the presence or absence of oxygen gas. The disappearance of the visible absorption at 450 and 412 nm after the zwitterionic solution has been exposed to light leads one to conclude that the W-I bond has been broken since carbonyl complexes containing metal-halogen bonds are colored while those containing only phosphines are colorless.

The UV-visible spectral data of the zwitterionic complexes is shown in Table IV. The striking feature of these data as with the carbonyl stretching frequencies is the fact that the absorption for the iodo, bromo, and

INFRARED CARBONYL STRETCHING SPECTRA OF $\text{W}(\text{CO})_4 \text{I}^- [\text{C}_6\text{H}_5]_2 \text{PCH}_2 \text{P}^+ [\text{C}_6\text{H}_5]_2 \text{CH}_3$ BEFORE
 LIGHT EXPOSURE (top), AFTER ONE HOUR, AND AFTER SEVERAL HOURS IN SUNLIGHT; ALL IN CH_2Cl_2

ULTRAVIOLET VISIBLE SPECTRA OF $\text{W(CO)}_4\text{I}^-\text{[C}_6\text{H}_5\text{]}_2\text{PCH}_2\text{P}^+\text{[C}_6\text{H}_5\text{]}_2\text{CH}_3$
BEFORE(left) AND AFTER(right) EXPOSURE TO LIGHT.

chloro complexes are very nearly the same. In fact through the series Cl, Br and I there is a shift to higher energy. This shift is quite odd since for most transition metal complexes containing these halides there is a shift to lower energies. McLean, however, has reported a shift similar to what is observed here for the complexes $(R_4N)^+(W(CO)_5X)^-$ in which X = Cl, Br, and I.²¹ Carbonyl halide complexes of various transition metals give rise to absorption in the visible spectrum which are most often charge transfer bands. The intensities observed for the zwitterionic complexes are too large to be d-d transitions. It is reasonable to assume that the charge transfer is either a ligand to ligand type (p_π orbital of halogen to p_π^* of CO) or a metal to ligand type (orbital mostly metal d in character to a p_π^* of a carbonyl). A hypsochromic shift is observed for $I(OC)_4^-\overset{+}{W}PPh_2CH_2CH_2PPh_2CH_3$ as the polarity of the solvent increases (Figure 18, Table V). This indicates that the difference in energy between the ground and excited state has increased. This could result if the ground state is lowered relative to the excited or if the excited state is elevated relative to the ground state. A polar solvent would be likely to interact more strongly with the iodo ligand than a nonpolar solvent. A transition from an orbital which is mostly halogen in character to an antibonding CO orbital is consistent with the blue shift. Solvent shift studies were not conducted on the chloro and $I(CO)_4^-\overset{+}{W}PPh_2CH_2CH_2PPh_2CH_3$ zwitterionic complexes.

TABLE IV

Ultraviolet/Visible Spectral Data for the Zwitterions in nm (cm^{-1})

				Solvent
$\text{IW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3$	450 (22222)	412 (24271)	244 (40983)	CHCl_3
$\text{IW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3$	444 (22522)	408 (24509)	244 (40983)	CH_2Cl_2
$\text{IW}(\text{CO})_4\text{PPh}_2(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3$	442 (22624)	406 (24631)	229 (43668)	CH_2Cl_2
$\text{BrW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{C}_2\text{H}_5$	459 (21786)	414 (24154)	231 (43290)	CH_2Cl_2
$\text{ClW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{C}_3\text{H}_7$	458 (21834)	416 (24038)	231 (43291)	CH_2Cl_2

TABLE V

Hypsochromic Solvent Induced Shift in nm (cm^{-1})

<u>Solvent</u>	$\text{I(OC)}_4 \overset{-}{\text{WPPh}}_2 \text{CH}_2 \overset{+}{\text{PPh}}_2 \text{CH}_3$	$\text{Br(OC)}_4 \overset{-}{\text{WPPh}}_2 \text{CH}_2 \overset{+}{\text{PPh}}_2 \text{C}_2\text{H}_5$
Benzene	413 (24215)	418 (23923)
Chloroform	412 (24271)	415 (24096)
Dichloromethane	408 (24509)	414 (24154)
Acetone	405 (24691)	412 (24271)
Methanol	403 (24813)	411 (24330)

A mass spectrum of $\text{I(OC)}_4 \overset{-}{\text{WPPh}}_2 \text{CH}_2 \overset{+}{\text{PPh}}_2 \text{CH}_3$ (Figure 19) showed no mass larger than 303 while the molecular weight of the complex is 822.

ULTRAVIOLET/VISIBLE SPECTRA OF IODO DIPHENYLPHOSPHINOMETHYLDIPHENYLPHOSPHONIUMMETHANETETRACARBONYLTUNGSTEN(0)
IN FOUR SOLVENTS

1 CHLOROFORM

2 ACETONE

3 METHANOL

4 BENZENE

Summary and Suggestions for Future Work

The zwitterions reported in this thesis are the first to be reported in which the metal is in a zero oxidation state. They seem to have unusual stability in comparison to other carbonyl halides. $(R_4N)^+(W(CO)_5X)^-$ complexes decompose in air rather quickly while the zwitterions reported here are stable in air indefinitely. The greater stability of $I(OC)_4WPPh_2CH_2^+PPh_2CH_3^-$ as compared to $(R_4N)^+(W(CO)_5X)^-$ may occur because $(R_4N)^+$ is not a sufficiently large cation to stabilize the lattice. Perhaps intraelectrostatic interaction gives the zwitterion extra stability.

It would be of interest to synthesize $((OC)_4IWPPh_3)^-(R_4P)^+$ and compare its stability to the zwitterion.

Reactions of the zwitterion should be investigated and perhaps stable group VI B complexes containing metal-alkyl bonds could be synthesized. For example the reaction

might serve as a route to such complexes.

CHAPTER III

EXPERIMENTAL SECTION

General Considerations

All microanalyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Proton nuclear magnetic resonance spectra of concentrated deuteriochloroform solutions were obtained with a Varian T-60 spectrometer. The spectrum of $\text{I}(\text{CO})_4\text{W}^-\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3$ was obtained with a Varian HA 100 spectrometer at the University of Illinois. Tetramethylsilane was used as an internal standard for all the spectra.

The infrared spectra were recorded with a Perkin-Elmer 337 grating spectrophotometer and expanded with an E. H. Sargent SR recorder. The calibration peaks (not shown on diagrams) are those of polystyrene at 2850.7 cm^{-1} , after the first calibration peak is recorded the polyethylene standard is exchanged for the sample and the process is allowed to go until the 1700 cm^{-1} region is reached, then once again the exchange in the sample beam is performed; this time the sample is removed and the polystyrene standard is returned to the sample beam compartment. The spectra are considered to be accurate to $\pm 2\text{ cm}^{-1}$.

All melting and decomposition temperatures were taken on an Arthur H. Thomas Unimelt apparatus and are reported uncorrected.

The ultraviolet-visible spectra were measured on a Beckman DB-G spectrophotometer and recorded on Beckman 10" recorder.

The mass spectrum of $\text{IW}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{CH}_3$ was recorded on a Du Pont Instruments 21 490 mass spectrometer.

All high pressure reactions were performed in a Parr Instrument 425 HC pressure bomb.

Phosphines were purchased from Pressure Chemical Co.

Drawings of special glassware are shown in Appendix I.

Procedure for Drying Tetrahydrofuran²²

To the desired volume of tetrahydrofuran, in a refluxing apparatus, freshly cut strips of sodium metal were added and ten grams of benzophenone was dissolved. This mixture was gently refluxed under a nitrogen atmosphere until the solution turned deep blue and was then distilled.

Procedure for Purifying Tungstenhexacarbonyl

In a sublimation vessel the desired amount of tungstenhexacarbonyl was heated to 60°C at 0.05 torr until most of it was on the "cold finger."

Preparation of Ligands1-diphenylphosphino,1-methyldiphenylphosphonium-methane iodide

In a round bottom flask, supported by a magnetic stirrer, 3.17 g (8 mmol) of 1,1-bis(diphenylphosphino)methane was dissolved in 100 ml of benzene. To this solution 0.65 ml (10 mmol) of iodomethane was added with a syringe and stirred for 2 hr with moderate heating (35–40°C). during this time the solution turned cloudy and a fine precipitate was formed. After 2 hr the powder was collected on a medium fritted filter, washed twice with benzene and twice with petroleum ether (30–60°) and allowed to air dry. This crude product was recrystallized from absolute methanol to yield 2.87 g (69%) of pure material (mp 172–174°C).

1-diphenylphosphino,2-methyldiphenylphosphonium-ethane iodide

The method described above was tried but it produced the di-quaternized phosphonium salt, $\text{CH}_3\overset{+}{\text{PPh}_2}(\text{CH}_2)_2\overset{+}{\text{PPh}_2\text{CH}_3} \overset{-}{2\text{I}}$. The white solid melted at 281–283°C.

The monoquaternized product was prepared in the following way: In a round bottom flask, supported by a magnetic stirrer, 8.0 g (20 mmol) of 1,2-bis(diphenylphosphino)ethane was dissolved in 100 ml of benzene and 1.25 ml (20 mmol) of iodomethane in 100 ml of benzene was added via a dropping funnel over a period of 2 hr. During this addition a fine white precipitate formed.

This precipitate was collected after 3 hr, washed twice in benzene and twice in petroleum ether (30-60°) to yield the crude product (mp 156-166°C).

Chloroform/methanol, dichloromethane/n-propanol, acetone/hexane, and dichloromethane/benzene were tried as recrystallization solvents with no success. An oil would always precipitate out of the solution. This oil, once dried under high vacuum, would become an amorphous solid with a wide melting range (89-108°C). The crude product yield was 54%.

1-diphenylphosphino,1-ethyldiphenylphosphonium-methane bromide

In a round bottom flask 4.0 g (10 mmol) of 1,1-bis(diphenylphosphino)methane and an excess (0.9 ml) of bromoethane were heated, with stirring, in 50 ml of benzene at 40°C for 4 to 6 hr. Upon cooling the solution became cloudy and white precipitate formed. This powder was collected on a frit of medium porosity and washed with benzene and petroleum ether (30-60°). The crude product was then dissolved in a minimum volume of hot absolute methanol and this volume was further reduced by means of rotary vacuum evaporator until a heavy oil remained. Benzene was added to this oil and after 10 hr large crystals formed. After 86 hr all the oil had become crystalline, the crystals themselves were large (4-6 mm) and regular, however their nmr spectrum showed benzene to be trapped in the lattice; hence the

crystals were ground in a mortar and dried under high vacuum for 12 hr. A 49% yield of product was obtained (mp 154-156°C).

1-diphenylphosphino,1-propyldiphenylphosphonium-methane chloride

To 30 ml of dry tetrahydrofuran, 4.0 g (10 mmol) of 1,1-bis(diphenylphosphino)methane and 1.0 ml (10 mmol) of chloropropane were added. This solution was refluxed under a nitrogen atmosphere for 10 to 12 hr. Upon cooling no precipitate was formed. The solvent was removed by means of rotary vacuum evaporation. The residual white powder had a wide melting range. The powder was placed on a fritted funnel and washed with absolute methanol (100 ml), the insoluble portion, which remained on the fritt was the starting material. Upon stripping the solvent, the desired product was obtained as a creamy oil. Attempts at recrystallization, with the usual solvents, were unsuccessful. The product was dried under high vacuum for 48 hr to produce a 38% yield of the impure product (mp 140-160°C).

Preparation of Monosubstituted Pentacarbonyltungsten(0)
Complexes, the 1:1 Electrolytes

[1-diphenylphosphino,1-methyldiphenylphosphonium-methane] -
pentacarbonyltungsten(0) iodide

In a photolysis reaction vessel 3.3 g (9 mmol) of tungstenhexacarbonyl was added to approximately 200 ml of dry tetrahydrofuran and irradiated with ultraviolet light for 7 hr under a nitrogen atmosphere. To the ensuing olive green solution 2.33 g (4.4 mmol) of $\text{PPh}_2\text{CH}_2\overset{+}{\text{PPh}_2\text{CH}_3}\overset{-}{\text{I}}$ was added and stirred for 2 hr. The yellow solution was first filtered to remove unreacted tungstenhexacarbonyl. The solvent was removed by means of a rotary vacuum evaporator and further purified by removing the unreacted tungstenhexacarbonyl under a high vacuum at 60°C for 5 hr. The sublimed W(CO)_6 may now be used again as it is in a pure crystalline form. The remainder of the yellow powder was recrystallized from dichloromethane/absolute methanol to produce 3.45 g (89% yield) of the desired pure complex (decomp. 159-161°C; Lit.,¹ 145-150°C).

[1-diphenylphosphino,2-methyldiphenylphosphonium-ethane] -
pentacarbonyltungsten(0) iodide

An excess of tungstenhexacarbonyl (4 g) was added to 200 ml of dry tetrahydrofuran in the above mentioned photolysis apparatus and irradiated with ultraviolet light for

7 hr under a nitrogen atmosphere. To the olive green solution 2.96 g (5.5 mmol) of $\text{PPh}_2(\text{CH}_2)_2\text{P}^+\text{Ph}_2\text{CH}_3^- \text{I}^-$ was added and stirred for several hours. The yellow solution was filtered, evaporated to dryness, cleansed of $\text{W}(\text{CO})_6$ by means of high vacuum sublimation and recrystallized from dichloromethane/n-propanol to produce a cream colored powder (87% yield) (decomp. 153–158°C). Calcd. for $\text{WIP}_2\text{O}_5\text{C}_{32}\text{H}_{27}$: C, 44.47; H, 3.16; I, 14.68; P, 7.17 Found: C, 42.47; H, 3.25; I, 13.65; P, 6.46

[1-diphenylphosphino,1-ethyldiphenylphosphonium-methane]-pentacarbonyltungsten(0) bromide

An excess of tungstenhexacarbonyl (4 g) was added to 250 ml of dry tetrahydrofuran in the above mentioned photolysis apparatus and irradiated with ultraviolet light for 7 hr under a nitrogen atmosphere. To the olive green solution 1.20 g (2.5 mmol) of $\text{PPh}_2\text{CH}_2\text{P}^+\text{Ph}_2\text{C}_2\text{H}_5^- \text{Br}^-$ was added and stirred for 3 hr. The yellow solution was filtered, solvent stripped, cleansed of $\text{W}(\text{CO})_6$ by high vacuum sublimation and recrystallized from dichloromethane/absolute ethanol to produce 1.6 g (68% yield) of the desired product (mp 187–189°C). Calcd. for $\text{WBrP}_2\text{O}_5\text{C}_{32}\text{H}_{27}$: C, 47.03; H, 3.33; P, 7.58; Br, 9.70 Found: C, 45.37; H, 3.58; P, 7.14; Br, 8.90

Preparation of Zwitterions

Iodo(diphenylphosphinomethyl)diphenylphosphoniummethane)- tetracarbonyltungsten(0)

Into an oxygen free refluxing apparatus 40 ml of diglyme and 0.52 g (6 mmol) of the pentacarbonyl complex precursor were added and heated to 160°C over a period of 2 hr, with stirring. At 158° all the solid had dissolved into the diglyme and CO evolution was moderate. Upon reaching 160° the heating was discontinued and the system was allowed to reach room temperature slowly. During cooling a light green precipitate formed and this precipitate was collected on a frit of medium porosity, washed twice with benzene and twice with petroleum ether (30–60°) to produce 0.36 g (70% yield) of the desired zwitterion (decomposition 190–192°C with CO evolution at 204°C). Calcd. for $\text{WIP}_2\text{O}_4\text{C}_{30}\text{H}_{25}$: C, 43.83; H, 3.07; I, 15.44; P, 7.55; W, 22.34
Found: C, 43.49; H, 2.95; I, 15.21; P, 7.44; W, 22.28

Iodo(diphenylphosphinomethyl)diphenylphosphoniummethane)- tetracarbonyltungsten(0)

In the above mentioned refluxing apparatus 30 ml of diglyme and 2.29 g (2.7 mmol) of the pentacarbonyl complex precursor were slowly heated to 160° over a period of 2 hr with stirring and under a nitrogen atmosphere. At 159° CO evolution ceased and the heating was discontinued. The

apparatus was allowed to cool to room temperature. During cooling a precipitate was formed and at 26° it was collected on a fritt of medium porosity and washed with several portions of petroleum ether (30-60°) to produce 1.82 g (80% yield) of the desired zwitterion (decomposition 188-196°C). Calcd. for $\text{WIP}_2\text{O}_4\text{C}_{31}\text{H}_{27}$: C, 44.52; H, 2.26; I, 15.17; P, 7.41 Found: C, 43.79; H, 3.41; I, 15.12; P, 6.89

Bromo(diphenylphosphinoethyldiphenylphosphoniummethane)tetracarbonyltungsten(0)

In the previously mentioned refluxing apparatus 20 ml of diglyme and 0.47 g (6 mmol) of the pentacarbonyl-complex precursor were slowly heated to 145° with stirring under a nitrogen atmosphere. At 142° CO evolution stopped and heating was discontinued, the solution was allowed to cool slowly and in this process precipitate formed. This precipitate was collected on a fritt of medium porosity and washed several times with 10 ml volumes of petroleum ether (30-60°) to produce 0.12 g (27% yield) of the desired zwitterionic complex (decomposition 186-189°C).

Chloro(diphenylphosphinopropyldiphenylphosphoniummethane)-
tetracarbonyltungsten(0)

An excess of tungstenhexacarbonyl (4 g) was added to 300 ml of dry tetrahydrofuran in the photolysis apparatus and irradiated with ultraviolet light for 7 hr under a nitrogen atmosphere. To the olive green solution 1.63 g (3.5 mmol) of $\text{PPh}_2\text{CH}_2\overset{+}{\text{P}}\text{Ph}_2\text{C}_3\text{H}_7 \overset{-}{\text{Cl}}$ was added and stirred for several hours.

The above mentioned procedures for purification and recrystallization were applied to the ensuing yellow solution and 2.97 g (89% yield) of the zwitterion was obtained. The decomposition range for the product was found to be 179-185°C.

Iodo(diphenylphosphinomethyldiphenylphosphoniummethane)tetracarbonyltungsten(0) and Bromo(diphenylphosphinoethyldiphenylphosphoniummethane)tetracarbonyltungsten(0)

In a refluxing apparatus 3.5 g (10 mmol) of tungstenhexacarbonyl was dissolved in excess (20 ml) of acetonitrile and refluxed for 42 hr under a nitrogen atmosphere to give $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$.²³ After this time 2.5-norbornadiene was added in excess and the mixture stirred for 3 hr.²⁴ This air stable mixture was filtered to remove unreacted solids, heated to 80° to boil off excess acetonitrile and then

refluxed with either the phosphonium iodide or the phosphonium bromide salt for 2 hr at 70°. Upon cooling the solution, a light green precipitate formed which was collected on a frit and washed with benzene and petroleum ether (30-60°), and recrystallized from dichloromethane/absolute methanol. Calcd. for $\text{WIP}_2\text{O}_4\text{C}_{30}\text{H}_{25}$: C, 43.83; H, 3.07; P, 7.55; I, 15.44 Found: C, 43.50; H, 3.23; P, 6.13; I, 15.37

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APPENDIX I

General view of the photolysis apparatus.

Cross section of the photolysis apparatus.

Pyrolysis apparatus for the conversion of 1:1 electrolytes.

Cross section of the sublimation vessel.

The conductance cell.

CROSS SECTION OF THE
PHOTOLYSIS APPARATUS

Cavity for the light
source

Water jacket

Carbonyl and THF
solution

Magnetic stirrer

N_2

APPARATUS FOR CONVERTING
PRECURSORS TO ZITTERIONS

CROSS SECTION OF THE SUBLIMATION APPARATUS

CELL FOR THE CONDUCTANCE MEASUREMENTS

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