Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

CHEMISTRY OF THE CYCLOPENTADIENYLMETAL CARBONYLS V*. (A) REACTIONS OF CYCLOPENTADIENYLMOLYBDENUM AND -TUNGSTEN TRICARBONYL HALIDES WITH GROUP VA DONOR LIGANDS
(B) CATIONIC CYCLOPENTADIENYLMOLYBDENUM AND -TUNGSTEN CARBONYL DERIVATIVES WITH GROUP VA DONOR LIGANDS

P. M. TREICHEL, K. W. BARNETT AND R. L. SHUBKIN
Department of Chemistry, University of Wisconsin, Madison, Wisconsin

(Received April 29th, 1966; in revised form June 13th, 1966)

INTRODUCTION

Few substitution reactions of the cyclopentadienylmolybdenum and -tungsten tricarbonyl halides are now known though such reactions with metal carbonyl halides have been extensively studied[2]. Tris(dimethylamino)phosphine (tdp) and $C_5H_5Mo(CO)_3I$ gives two isomeric compounds $C_5H_5Mo(CO)_2(tdp)I$[3]. Reactions of $C_5H_5W(CO)_3Cl$ and both triphenylphosphine and triethylphosphine have been reported; the former reaction leads to only one product $C_5H_5W(CO)_2[(C_6H_5)_3P]Cl$ whereas the latter gives the two compounds[4] $C_5H_5W(CO)_2[(C_2H_5)_3P]Cl$ and $C_5H_5W(CO)_2[(C_2H_5)_3P]_2^+Cl^-$. Reactions of $C_5H_5M(CO)_3Cl$ ($M = Mo^5, W^4$) with ammonia and hydrazine give exclusively the ionic derivatives $C_5H_5M(CO)_3(NH_3)^+$-Cl^- and $C_5H_5M(CO)_3(N_2H_4)^+Cl^-$.

There are three points of interest concerning substitution reactions of cyclopentadienylmolybdenum and -tungsten tricarbonyl halides. First, the question of whether an ionic species $[C_5H_5M(CO)_3L^+X^-]$ or an uncharged species $[C_5H_5M(CO)_2LX]$ will be formed has not been evaluated in the work to date. Second, the number of carbonyls that can be substituted by other donor ligands is of interest. Third, the possibility exists that isomeric species differing in the orientation of the respective groups bonded to the metal will be formed; this possibility is realized only in the complexes of tdp[3]. We felt that a more detailed study of substitution reactions of these cyclopentadienyl metal carbonyl halides would now be valuable to provide more background information to judge these criteria. This paper describes substitution reactions of the cyclopentadienylmetal tricarbonyl halides with triphenylphosphine, -arsine, -stibine, and with 1,2-bis(diphenylphosphino)ethane (diphos), and with the nitrogen bases 2,2'-bipyridine (bipy) and *o*-phenanthroline (*o*-phen).

The ionic cyclopentadienylmetal carbonyls $C_5H_5M(CO)_4^+X^-$ ($M = Mo, W$) were first reported by Fischer and coworkers[6] in 1962, subsequent to the description of the related π-ethylene derivatives $C_5H_5M(CO)_3(\pi\text{-}C_2H_4)^+X^-$ ($M = Mo, W$)[7]. Since that time several other species related to the parent cation have also been

---

* Part IV, see ref. 1.

described[4,5,8,9]. In the course of this work we also studied reactions leading to the formation of the related ionic species $C_5H_5M(CO)_nL_{4-n}^+X^-$ (M = Mo, W; L = triphenylphosphine, -arsine, and acetonitrile) by the reactions of the cyclopentadienylmetal carbonyl halide ($C_5H_5M(CO)_nL_{3-n}X$), a donor molecule, and an aluminum halide.

EXPERIMENTAL

Cyclopentadienylmolybdenum tricarbonyl dimer[10] and cyclopentadienylmolybdenum tricarbonyl chloride and bromide[11] were prepared by methods well established in the literature. Cyclopentadienylmolybdenum tricarbonyl iodide was prepared by cleaving cyclopentadienylmolybdenum tricarbonyl dimer with iodine in chloroform solution. Tungsten analogs of the above were prepared by identical routes.

Infrared spectra of the compounds prepared here were run on a Beckman IR-10 grating spectrometer. Analyses were performed by Alfred Bernhardt Laboratories, Mülheim, Germany, and Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. Molecular weights were determined with a Mechrolab Vapor Pressure Osmometer as approximately 0.05 molal solutions in benzene.

All operations were carried out routinely under an atmosphere of nitrogen, including admission of nitrogen to evacuated flasks and collection of samples under nitrogen during chromatography. The products described are all stable in air in the solid state but somewhat less stable in solution. The ionic compounds $C_5H_5M(CO)_nL_{4-n}^+PF_6^-$ were somewhat sensitive to light and were stored in the dark.

Acid washed aluminum oxide (Merck) was utilized for chromatographic separations.

(A) Reactions of cyclopentadienylmolybdenum and tungsten tricarbonyl halides with Group VA ligands

The reaction conditions for all of the reported reactions were the same. The cyclopentadienylmolybdenum or -tungsten carbonyl halide and an excess of the desired ligand were dissolved in 75–100 ml of benzene and refluxed for 18 h under nitrogen. The reaction mixtures were filtered while hot to remove the insoluble ionic species and any products of decomposition which formed in the reaction. The filtrates were evaporated using a rotary evaporator, and if the infrared spectrum of the resulting residue indicated the presence of a covalent substitution product, chromatography on alumina with benzene as eluent was employed. The general order of elution observed was: 1. $C_5H_5M(CO)L_2X$ (if present); 2. $C_5H_5M(CO)_2LX$; 3. $C_5H_5M(CO)_3X$. These individual products were then purified by crystallization from a mixture of chloroform and petroleum ether.

If ionic species were isolated in the initial filtration, these compounds were dissolved from the filter in water and precipitated as hexafluorophosphate salts by addition of a saturated solution of ammonium hexafluorophosphate. Final purification was effected by crystallization of these substances from an acetone/ether mixture.

The products obtained in each reaction ,with respective properties, yields, and analyses are given in Table 1.

(B) Cationic cyclopentadienylmolybdenum and -tungsten carbonyl derivatives with group VA donor ligands

Reaction of $C_5H_5Mo(CO)_3Cl$, triphenylphosphine, and $AlCl_3$. A mixture of 1 g $C_5H_5Mo(CO)_3Cl$ (3.5 mmole), 0.88 g triphenylphosphine (3.5 mmole) and 0.75 g $AlCl_3$ (5.6 mmole) was refluxed in benzene for 16 h. The solution was cooled, and 50 ml of water was added. After stirring 15 min the mixture was filtered. The solid residue was dissolved in acetone, filtered, and an aqueous solution of NH_4PF_6 added dropwise. Yellow crystals (1.25 g) precipitated and were collected. Comparison of an infrared spectrum of this solid with known spectra of the pure compounds $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+ PF_6^-$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$ prepared below, showed this solid to be a mixture of these compounds. The benzene/water filtrate from above was separated; addition of NH_4PF_6 solution to the aqueous layer gave 0.15 g of a fine, yellow powder, identified as $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6^-$. The benzene layer was dried over Na_2SO_4 and then evaporated to dryness to give 0.3 g $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$.

An analogous reaction between $C_5H_5Mo(CO)_3I$, triphenylphosphine, and $AlCl_3$ gave the mono- and bistriphenylphosphine substituted cations as well as $C_5H_5Mo(CO)_2[(C_6H_5)_3P]I$.

Though presumably the solubility difference between the chloride salts of the cations would have allowed their complete separation, this separation was not attempted since the pure products could be obtained in specific reactions.

Preparation of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6^-$. A mixture of 0.5 g $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$ (0.95 mmole) and 0.25 g $AlCl_3$ (1.9 mmole) in 20 ml benzene was heated to 70° for 16 h under an atmosphere of 1200 psi of carbon monoxide in a glass-lined steel autoclave. The reaction mixture was then removed from the autoclave and cooled to 0°. Cold aqueous NH_4PF_6 solution was added with vigorous stirring. Yellow crystals formed and were filtered off. Recrystallization of this solid from acetone and ether gave 0.25 g of $C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6^-$ (yield 40.5%).

Preparation of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$. One g $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$ (1.9 mmole), 1.0 g triphenylphosphine (3.8 mmole) and 0.51 g $AlCl_3$ (3.8 mmole) were refluxed in 50 ml benzene for 20 h. The mixture was cooled and 50 ml of H_2O was slowly added. Filtration gave a yellow solid which was dissolved in 20 ml of acetone and filtered. Aqueous NH_4PF_6 solution was added dropwise to the acetone solution until no more precipitation was observed to occur. The yellow crystals were filtered, and then recrystallized from acetone and ether, and dried to give 1.1 g of product (yield 66%).

The benzene filtrate from above was separated, dried and concentrated to give 0.3 g of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$ (recovery 30%).

Reaction of $C_5H_5W(CO)_3Cl$, triphenylphosphine and $AlCl_3$. This reaction was run in a manner identical to that described above for the molybdenum compound. From the reaction of 1.0 g $C_5H_5W(CO)_3Cl$ (2.7 mmole), 1.42 g $AlCl_3$ (2.7 mmole) and 1.42 g triphenylphosphine (5.4 mmoles) was isolated 0.45 g $C_5H_5W(CO)_2[(C_6H_5)_3P]Cl$ (yield 28%), 0.45 g $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6^-$, (yield, 22.5%), and 1.4 g of a mixture of the two compounds $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6^-$ and $C_5H_5W(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$. An analysis for the pure salt $C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6^-$ was obtained.

TABLE 1

PRODUCTS FROM REACTIONS OF $C_5H_5M(CO)_3X$ (M = Mo, W) AND GROUP V LIGANDS

Compound, color	*Yield (%)*	*M.p.*^{a} *(°C)*	*CO stretch (cm^{-1})*^{b}		*C*^{d}*(%)*	*H(%)*	*L*^{e}*(%)*	*X*^{f}*(%)*	*Mol.wt.*
$C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$	14	185°	1975(vs)	calcd.	58.25	3.88	6.21	6.89	515
orange			1885(vs)	found	57.86	4.37	6.11	7.32	506
$C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$	6.8	178°	1795(vs)	calcd.	66.40	4.61	8.16	4.74	759
orange				found	65.31	4.58	7.40	4.18	771
$C_5H_5Mo(CO)_2[(C_6H_5)_3P]Br$	45	163°	1980(vs)	calcd.	53.67	3.58	5.55	14.31	559
orange			1890(vs)	found	53.41	3.57	6.24	15.09	567
$C_5H_5Mo(CO)[(C_6H_5)_3P]_2Br$	trace		1802(vs)						
orange									
$C_5H_5Mo(CO)_2[(C_6H_5)_3P]I$	57	181°	1972(vs)	calcd.	49.50	3.30	5.12	20.72	606
red			1890(vs)	found	49.49	3.17	5.35	20.87	615
$C_5H_5Mo(CO)_2[(C_6H_5)_3As]Cl$	32	154°	1964(vs)	calcd.		3.58	13.44	6.36	558
orange			1865(vs)	found		3.26	12.36	6.03	543
$C_5H_5Mo(CO)_2[(C_6H_5)_3As]Br$	32	147°	1978(vs)	calcd.	49.75	3.32	12.44	13.27	603
orange			1890(vs)	found	49.51	3.41	11.56	13.02	611
$C_5H_5Mo(CO)_2[(C_6H_5)_3As]I$	38	151°	1975(vs)	calcd.	46.15	3.08	11.54		650
red			1890(vs)	found	45.98	3.04	11.36		629
$C_5H_5Mo(CO)_2[(C_6H_5)_3Sb]Cl$	9	155°	1975(vs)	calcd.	49.59	3.31		5.87	605
orange			1883(vs)	found	49.74	3.52		5.72	594
$C_5H_5Mo(CO)_2[(C_6H_5)_3Sb]Br$	9	170°	1980(vs)	calcd.	46.15	3.08		12.31	650
orange			1889(vs)	found	45.80	3.33		11.11	661
$C_5H_5Mo(CO)_2[(C_6H_5)_3Sb]I$	18	165°	1975(vs)	calcd.	43.04	2.87		18.22	697
red			1888(vs)	found	43.33	2.92		18.51	682
$C_5H_5W(CO)_2[(C_6H_5)_3P]Cl$	59	194°	1965(vs)	calcd.	49.83	3.32	5.15	5.81	602
orange			1872(vs)	found	49.64	3.57	5.73	6.52	592
$C_5H_5W(CO)_2[(C_6H_5)_3As]Cl$	37	165°	1962(vs)	calcd.	46.44	3.10	11.61	5.50	646
orange			1870(vs)	found	46.00	3.24	11.13	5.24	639
$C_5H_5W(CO)_2[(C_6H_5)_3Sb]Cl$	trace		1965(vs)						
orange			1870(vs)						
$C_5H_5Mo(CO)_2(diphos)^+PF_6^-$	73	137°	1995(vs)	calcd.	52.11	3.82	12.24	15.00	
yellow			1928(vs)^c	found	51.10	4.07	12.32	15.49	

$C_5H_5Mo(CO)(diphos)Cl$	11	189°	1845(vs)	calcd.	61.58	4.64		5.62	622
orange				found	60.33	4.85		5.76	631
$[C_5H_5Mo(CO)_2I]_2$-μ-diphos	trace		1965(vs)						
orange			1880(vs)						
$C_5H_5W(CO)_2(diphos)^+PF_6^-$	56	148°	1980(vs)	calcd.	46.70	3.42	10.97		
yellow			1905(vs)[c]	found	47.41	3.97	10.79		
$[C_5H_5W(CO)_2Cl]_2$-μ-diphos	8	209°	1962(vs)	calcd.	44.53	3.16	5.85	6.51	1078
orange			1868(vs)	found	44.39	3.60	6.24	6.85	1031
$C_5H_5Mo(CO)_2(bipy)^+PF_6^-$	82	280°d	1991(vs)	calcd.	39.38	2.51		22.01	
red			1914(vs)[c]	found	39.31	2.66		20.62	
$C_5H_5Mo(CO)_2$(*o*-phen)$^+PF_6^-$	82	280°d	1990(vs)	calcd.	42.07	2.40		21.03	
red			1915(vs)[c]	found	42.01	2.56		19.86	
$C_5H_5W(CO)_2(bipy)^+PF_6^-$	89	225°d	1980(vs)	calcd.	33.66	2.14	4.62		
red			1899(vs)[c]	found	33.75	1.88	4.84		
$C_5H_5W(CO)_2$(*o*-phen)$^+PF_6^-$	82	230°d	1984(vs)	calcd.	36.19	2.06	4.44		
red			1901(vs)[c]	found	36.08	1.96	4.22		

---

[a] Determined *with a Kofler Micro Stage* melting point apparatus. [b] KBr *solution cells* (0.1 *mm*) empolyed in all cases, with chloroform as solvent, unless otherwise noted. [c] Dichloromethane solution. [d] Occasionally extremely large and random deviations from calculated values were obtained in carbon analyses, though other analyses on the same sample for H, halogen, and P, As, or N were correct. We suspect that this is a result of the nature of the compound, which led to incomplete combustion; perhaps metal carbide formation could explain this result. [e] L = P, As, or N. [f] X = F, Cl, Br, or I.

Again it appears likely that these two chloride salts could have been separated but this did not prove necessary since the preparation of the pure salt described below could be easily accomplished.

Preparation of $C_5H_5W(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$. A mixture of 6.0 g $C_5H_5W(CO)_2[(C_6H_5)_3P]Cl$ (10.0 mmole), 5.24 g triphenylphosphine (20 mmole) and 2.7 g $AlCl_3$ (20 mmole) was refluxed in 100 ml benzene for 16 h. The yellow product $C_5H_5W(CO)_2[(C_6H_5)_3P]_2^+Cl^-$ precipitated and was filtered off. This solid was dissolved in water, filtered and the cation precipitated as the hexafluorophosphate salt on addition of a saturated NH_4PF_6 solution. The solid was filtered and dried and then recrystallized from an acetone/ether mixture (yield 8.55 g, 88%).

Preparation of $C_5H_5Mo(CO)_3[(C_6H_5)_3As]^+PF_6^-$. A mixture of 1.0 g $C_5H_5Mo(CO)_3Cl$ (3.5 mmole), 0.82 g triphenylarsine (2.68 mmole) and 0.75 g $AlCl_3$ (5.62 mmole) was stirred in 50 ml benzene at room temperature for 24 h. Then 50 ml of water was added and the mixture was stirred for 30 min. The mixture was filtered, giving a yellow solid which was dissolved in acetone; addition of aqueous NH_4PF_6 solution gave yellow crystals (0.3 g). The filtrate was separated into benzene and aqueous layers. The benzene layer yielded 0.5 g of a mixture of $C_5H_5Mo(CO)_3Cl$ and $C_5H_5Mo(CO)_2[(C_6H_5)_3As]Cl$ which was not separated. Addition of an NH_4PF_6 solution to the aqueous layer gave an additional 0.17 g of yellow crystals of the ionic compound (yield, 0.47 g, 25%). The sample was purified by recrystallization from acetone/ether.

Preparation of $C_5H_5W(CO)_3[(C_6H_5)_3As]^+PF_6^-$. This preparation was carried out in a manner similar to that described for the molybdenum compound, using 1.0 g $C_5H_5W(CO)_3Cl$ (2.72 mmole), 0.83 g of triphenylarsine (2.72 mmole) and 0.36 g $AlCl_3$ (2.72 mmole).

The yellow solid, $C_5H_5W(CO)_3[(C_6H_5)_3As]^+PF_6^-$, was recrystallized from acetone and ether (yield 0.2 g, 9.4%).

Preparation of $C_5H_5Mo(CO)_2[(C_6H_5)_3As]_2^+PF_6^-$. The reaction of 0.8 g $C_5H_5Mo(CO)_2[(C_6H_5)_3As]Cl$ (1.40 mmoles), 1.3 g triphenylarsine (4.3 mmole) and 0.57 g $AlCl_3$ (4.3 mmole) was carried out at room temperature for 16 h in 50 ml benzene. Water (50 ml) was added and the mixture stirred for 10 min. Filtration gave a yellow residue which was dissolved in acetone and converted to the insoluble PF_6^- salt on addition of aqueous NH_4PF_6 solution. This gave 0.05 g yellow crystals, which were recrystallized from acetone and ether (yield 3.6%).

The benzene layer from the filtrate yielded 0.25 g starting material.

Preparation of $C_5H_5W(CO)_2[(C_6H_5)_3As]_2^+PF_6^-$. The reaction of 0.8 g $C_5H_5W(CO)_2[(C_6H_5)_3As]Cl$ (1.24 mmole), 1.14 g triphenylarsine (3.72 mmole) and 0.5 g $AlCl_3$ (3.72 mmole) in benzene was carried out in the manner described for the analogous molybdenum reaction. This reaction gave 0.2 g of yellow crystalline $C_5H_5W(CO)_2[(C_6H_5)_3As]_2^+PF_6^-$ (yield 15.3%).

Preparation of $C_5H_5W(CO)_3[(C_6H_5)_3Sb]^+PF_6^-$. One g $C_5H_5W(CO)_3Cl$ (2.72 mmole), 2.0 g triphenylstibine (5.5 mmoles) and 0.72 g $AlCl_3$ (5.44 mmole) were refluxed in 50 ml benzene for 16 h. The reaction mixture was cooled in an ice bath and cold aqueous NH_4PF_6 solution added. Filtration of this solution gave 0.5 g brown solid residue. As much as possible of the residue was dissolved in acetone and filtered. Then ether was slowly added to filtrate until 0.05 g of yellow powder precipitated (yield 2.2%). Accurate elemental analyses were not obtained for this compound;

identification was made on the basis of its infrared spectrum.

Preparation of $C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+PF_6^-$. The compound $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$ (0.5 g, 0.66 mmole) was refluxed in 50 ml benzene with 3 ml CH_3CN (excess) and 0.26 g $AlCl_3$ (1.98 mmole) for 16 h. The solution was cooled and then shaken with aqueous NH_4PF_6 solution. No solid formation was observed. The two layers were separated and the yellow-orange benzene layer was dried over Na_2SO_4. After evaporation to a concentrated solution this material was chromatographed on alumina (Merck, acid washed) first using benzene/chloroform mixtures and finally pure chloroform as eluent. A single yellow band eluted which was crystallized from chloroform and hexane at −10°, giving 0.15 g of orange-yellow crystals. Contrary to what the solubility properties and behavior on chromatography would suggest, this compound was ionic, since it showed a very strong peak in the infrared at 835 cm^{-1} which was due to the PF_6^- ion. The analyses and spectra suggest the formulation $C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+PF_6^-$ (yield 24.4%).

Preparation of $C_5H_5Mo(CO)_2(CH_3CN)_2^+PF_6^-$. One g $C_5H_5Mo(CO)_3Cl$ (3.5 mmole) was refluxed for 16 h in 50 ml benzene with 1.5 g $AlCl_3$ (10.5 mmole) and 4 ml CH_3CN. At the end of this period the benzene was decanted from the red oil which had separated during the reaction. The oil was rinsed with small portions of benzene and then placed in an ice bath. Cold aqueous NH_4PF_6 solution was poured on the oil and the mixture stirred at 0° for 10 min. An orange solid formed which was filtered off and dried to give 1.2 g $C_5H_5Mo(CO)_2(CH_3CN)_2^+PF_6^-$ (yield 77%). Unfortunately the product could not be recrystallized without decomposition.

Preparation of $C_5H_5W(CO)_2(CH_3CN)_2^+PF_6^-$. The analogous reaction of 0.5 g $C_5H_5W(CO)_3Cl$ (1.36 mmole), 3 ml CH_3CN and 0.6 g $AlCl_3$ (4.5 mmole) was carried out in the manner described above, to give 0.50 g of product (yield 68%). Again, the orange crystals could not be recrystallized without decomposition.

DISCUSSION

In reactions of triphenylphosphine, -arsine, and -stibine with $C_5H_5Mo(CO)_3X$ (X = Cl, Br, I) and with $C_5H_5W(CO)_3Cl$ the only products obtained were covalent derivatives formed by substitution of the ligand for carbon monoxide. Interestingly only in the reaction $C_5H_5Mo(CO)_3Cl$ with triphenylphosphine was mono- and disubstitution observed; neither the other molybdenum halides nor $C_5H_5W(CO)_3Cl$ formed disubstitution products with this ligand*. Disubstitution products were not formed in reactions of triphenylarsine or -stibine ligands.

In no case did the infrared spectra or the behavior on chromatography suggest more than one isomer for products of the formula $C_5H_5M(CO)_2LX$. The two carbonyl bands in the infrared spectra were consistent in position and intensity in the series of compounds prepared here.

Covalent substitution products involving diphos were consistent with the above results in terms of the number of carbonyl groups displaced. From $C_5H_5Mo(CO)_3Cl$ and diphos the product $C_5H_5Mo(CO)(diphos)Cl$ was isolated in small yield. From the analogous reaction of $C_5H_5Mo(CO)_3I$ or $C_5H_5W(CO)_3Cl$ the only un-

---

* In one instance we observed what we believed to be the compound $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Br$ in an exceedingly small amount, but we were unable to duplicate this observation.

TABLE 2

CATIONIC CYCLOPENTADIENYLMETAL CARBONYL DERIVATIVES

Compound	*M.p.(°C)*	*CO stretch (cm⁻¹)*[a]		*C(%)*	*H(%)*	*L*[b]*(%)*	*F(%)*
$C_5H_5Mo(CO)_3[(C_6H_5)_3P]^+PF_6^-$	185°d	2025(s), 1995(m), 1955(s)	calcd.	47.87	3.09	9.49	
			found	48.13	3.01	9.36	
$C_5H_5Mo(CO)_3[(C_6H_5)_3As]^+PF_6^-$	223°	2040(s), 1995(m), 1960(vs)	calcd.	44.85	2.89		16.37
			found	44.68	2.85		15.85
$C_5H_5Mo(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$	255°	1975(s), 1895(vs)	calcd.	58.25	3.98	10.48	12.86
			found	58.16	4.13	10.31	13.03
$C_5H_5Mo(CO)_2[(C_6H_5)_3As]_2^+PF_6^-$	274°	1962(s), 1882(vs)	calcd.	53.00	3.60		11.70
			found	53.21	3.59		11.45
$C_5H_5Mo(CO)_2(CH_3CN)_2^+PF_6^-$	130–5°d	2000(s), 1900(s)	calcd.	[c]	2.50	6.31(N)	25.67
			found		2.70	6.40	26.47
$C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+PF_6^-$	139°	1860(s)	calcd.	[c]	4.26	1.56(N)	12.67
			found		3.87	1.58	12.44
$C_5H_5W(CO)_3[(C_6H_5)_3P]^+PF_6^-$	229°	2040(s), 1985(m), 1945(s)	calcd.	42.18	2.72	8.01	14.77
			found	42.18	2.72	8.42	15.56
$C_5H_5W(CO)_3[(C_6H_5)_3As]^+PF_6^-$	237°	2040(s), 1985(m), 1945(s)	calcd.	39.82	2.57		14.54
			found	39.80	2.52		13.62
$C_5H_5W(CO)_3[(C_6H_5)_3Sb]^+PF_6^-$		2060(s), 2000(s), 1982(s)					
$C_5H_5W(CO)_2[(C_6H_5)_3P]_2^+PF_6^-$	272°	1965(s), 1882(vs)	calcd.	52.99	3.62	9.54	11.70
			found	53.21	3.76	9.41	11.56
$C_5H_5W(CO)_2[(C_6H_5)_3As]_2^+PF_6^-$	270°	1965(s), 1885(vs)	calcd.	48.61	3.32		10.73
			found	48.46	3.35		10.70
$C_5H_5W(CO)_2(CH_3CN)_2^+PF_6^-$		1990(s), 1892(s)	calcd.	[c]	2.08	5.27(N)	21.43
			found		2.08	5.44	21.83

[a] Nujol mull spectra. [b] L = P, As, N. [c] See footnote *d*, Table 1.

charged product obtained ($[C_5H_5M(CO)_2X]_2$-μ-diphos) had the bifunctional phosphine bridging two metals; no mono-carbonyl species was found among the products.

In addition to the relatively small quantities of the above substances, the major product formed in each reaction of diphos was the ionic $C_5H_5M(CO)_2$-diphos$^+X^-$. This result was most interesting since none of the previous reactions with triphenylphosphine gave an analogous product. One must recall nonetheless that the ionic compound $C_5H_5W(CO)_2[(C_2H_5)_3P]_2^+Cl^-$ is a major product of the reaction of $C_5H_5W(CO)_3Cl$ and triethylphosphine[4]. One possible explanation for these results with triethyl- and triphenylphosphine involves the relative back-bonding capability of these ligands. Since reaction with a ligand with less back-bonding ability (viz., NH_3) apparently favors displacement of the halide ion rather than a carbonyl group one might predict that alkyl phosphines would be more likely to give the ionic product. Still, the extent of the differences between the reactions of diphos and those of triphenylphosphine, is surprising if interpreted solely on this basis. It seems likely that the chelating ability of the diphos ligand may be in someway involved also.

The chelating nitrogen ligands bipy and *o*-phen reacted rapidly with each of the cyclopentadienyl metal tricarbonyl halides to give exclusively the ionic products $C_5H_5M(CO)_2$bipy$^+X^-$ and $C_5H_5M(CO)_2$(*o*-phen)$^+X^-$. No covalent derivatives were formed in these reactions. However we observed that pyridine and $C_5H_5M(CO)_3Cl$ ($M = Mo, W$) gave no ionic product using reaction conditions similar to those employed in the above reactions. Small amounts of an unstable covalent derivative were sometimes observed, but this material was not characterized; decomposition was usually extensive in the reactions of pyridine in contrast to the results observed for bipy and *o*-phen. The difference between bipy and pyridine also suggests that the chelating ability of the ligand may be a predominate factor in the formation of an ionic species.

The reaction of cyclopentadienylmetal carbonyl halides, or metal carbonyl halides, with a halogen acceptor such as aluminum trichloride and a donor molecule is known to give ionic carbonyl species. Such reactions were used in the formation of the cationic species $C_5H_5M(CO)_4^+$ (ref. 6) and $C_5H_5M(CO)_3(C_2H_4)^+$ (ref. 7) ($M = Mo, W$). We have investigated such reactions as means of preparation of related species with group VA donor molecules when such species were not among the products of the direct ligand/$CpM(CO)_3X$ reaction. The following reactions were studied.

$$C_5H_5M(CO)_3Cl + AlCl_3 + L \rightarrow C_5H_5M(CO)_3L^+AlX_4^- + C_5H_5M(CO)_2L_2^+AlX_4^-$$

$$C_5H_5M(CO)_2LCl + AlCl_3 + L \rightarrow C_5H_5M(CO)_2L_2^+AlCl_4^-$$

$$C_5H_5M(CO)_2LCl + AlCl_3 + CO \rightarrow C_5H_5M(CO)_3L^+AlCl_4^-$$

$$M = Mo, W; \quad L = (C_6H_5)_3P, (C_6H_5)_3As, CH_3CN$$

Reactions were run in refluxing benzene or toluene under nitrogen. The crude reaction mixture was best hydrolyzed with ice-water to avoid decomposition. The cations could then be precipitated as the hexafluorophosphate salts from the aqueous solution. These crystalline salts were air stable, and soluble in polar organic solvents;

they were somewhat darkened by light over a prolonged period due to decomposition.

The initial reactions studied were between $C_5H_5Mo(CO)_3Cl$ and $C_5H_5W(CO)_3Cl$, triphenylphosphine, and $AlCl_3$. In both reactions two ionic products, $C_5H_5M(CO)_3[(C_6H_5)_3P]^+AlCl_4^-$ and $C_5H_5M(CO)_2[(C_6H_5)_3P]_2^+AlCl_4^-$, were obtained. Since the compounds $C_5H_5M(CO)_3Cl$ ($M = Mo, W$) both give substituted covalent derivatives $C_5H_5M(CO)_2[(C_6H_5)_3P]Cl$ with triphenylphosphine in refluxing benzene this compound is probably an intermediate in the formation of the disubstituted product. The complexes $C_5H_5M(CO)_3[C_6H_5)_3P]^+$ were inert to further substitution by triphenylphosphine under the reaction conditions.

$$\begin{tikzcd}
C_5H_5M(CO)_3Cl+(C_6H_5)_3P \arrow[r] \arrow[d, "(C_6H_5)_3P,\ AlCl_3"] & C_5H_5M(CO)_2[(C_6H_5)_3P]Cl \arrow[d, "(C_6H_5)_3P.\ AlCl_3"] \\
C_5H_5M(CO)_3[(C_6H_5)_3P]^+AlCl_4^- & C_5H_5M(CO)_2[(C_6H_5)_3P]_2^+AlCl_4^-
\end{tikzcd}$$

The same reaction with triphenylarsine gave only the monosubstituted compounds $C_5H_5M(CO)_3[(C_6H_5)_3As]^+AlX_4^-$ in accord with the lower reactivity of this ligand. The disubstituted ionic complex with this ligand could be obtained from the reaction of $C_5H_5M(CO)_2[(C_6H_5)_3As]Cl$, triphenylarsine and $AlCl_3$ however.

Reactions of $C_5H_5M(CO)_3Cl$, acetonitrile and $AlCl_3$ led to rather unstable disubstituted complexes $C_5H_5M(CO)_2(CH_3CN)_2^+AlX_4^-$. These materials must be hydrolyzed at 0° with an aqueous hexafluorophosphate solution if any product is to be obtained. Recrystallization without decomposition could not be accomplished.

We made several attempts to substitute a third ligand for carbon monoxide in these systems but in only one case was success achieved. The compound $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$ reacted with acetonitrile and $AlCl_3$ to give $C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+AlCl_4^-$. This material proved to be rather soluble in organic solvents and surprisingly was isolated by a process involving chromatography of the crude reaction product on alumina.

There was no evidence of more than one isomer being formed in reactions which gave disubstituted derivatives, though in theory the ligands L in the formula $C_5H_5M(CO)_2L_2^+$ might assume two orientations. One could not tell conclusively from the infrared spectra whether in different compounds different orientations were achieved.

The infrared spectra of the monosubstituted cations showed three carbonyl peaks at approximately 2030, 1990 and 1950 cm^{-1}. Substitution of a second ligand group for a carbonyl shifts the carbonyl absorption to still lower wave numbers; such compounds had two peaks at about 1970 and 1890 cm^{-1}. The compound $C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+PF_6^-$ has a single carbonyl stretching frequency at 1860 cm^{-1}. A similar progression in carbonyl stretching frequencies was also noted in the uncharged complexes. For $C_5H_5M(CO)_3X$ two peaks are observed at approximately 2040 and 1970 cm^{-1}. The monosubstitution products $C_5H_5M(CO)_2LX$ had carbonyl peaks near 1975 and 1890 cm^{-1} and the compound $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$ showed one absorption at 1795 cm^{-1}. Such a shift in carbonyl frequency is a general characteristic of series of compounds in which ligands with lower acceptor properties than CO are substituted for carbonyls.

ACKNOWLEDGEMENT

We wish to thank the Climax Molybdenum Co. for samples of the starting materials $Mo(CO)_6$ and $W(CO)_6$.

SUMMARY

The reaction of $C_5H_5Mo(CO)_3Cl$ and triphenylphosphine gives a mixture of $C_5H_5Mo(CO)_2[(C_6H_5)_3P]Cl$ and $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$; $C_5H_5Mo(CO)_3X$ ($X = Br, I$) and $C_5H_5W(CO)_3Cl$ react with triphenylphosphine giving monosubstitution only. With triphenylarsine and -stibine $C_5H_5M(CO)_3X$ ($M = Mo, X = Cl, Br, I$; $M = W, X = Cl$) monosubstitution is found to occur. The reaction of 1,2-bis(diphenylphosphino)ethane (diphos) and $C_5H_5Mo(CO)_3Cl$ gives $C_5H_5Mo(CO)(diphos)Cl$ and $C_5H_5Mo(CO)_2(diphos)^+Cl^-$. The reactions of $C_5H_5Mo(CO)_3I$ and $C_5H_5W(CO)_3Cl$ and diphos lead to $C_5H_5M(CO)_2(diphos)^+X^-$ and $[C_5H_5M(CO)_2X]_2$-μ-diphos.

The reactions of $C_5H_5Mo(CO)_3X$ ($X = Cl, Br, I$) and $C_5H_5W(CO)_3Cl$ and bipyridine (bipy) or *o*-phenanthroline (*o*-phen) give$C_5H_5M(CO)_2(bipy)^+X^-$ and $C_5H_5M(CO)_2(o\text{-phen})^+X^-$ ($M = Mo, W$) as the only products of these reactions. It is suggested that the chelating ability of a ligand is sometimes important in determining whether an ionic derivative is to be formed.

Reactions between the compounds $C_5H_5M(CO)_3Cl$ or $C_5H_5M(CO)_2LCl$ [$M = Mo, W$; $L = (C_6H_5)_3P, (C_6H_5)_3As$], a Group VA donor molecule or carbon monoxide, and $AlCl_3$ have been studied. From such reactions the compounds $C_5H_5M(CO)_3L^+AlCl_4^-$ and $C_5H_5M(CO)_2L_2^+AlCl_4^-$ [$M = Mo, W$; $L = (C_6H_5)_3P, (C_6H_5)_3As, CH_3CN$] were obtained. The compound $C_5H_5Mo(CO)(CH_3CN)[(C_6H_5)_3P]_2^+AlCl_4^-$ was obtained from $C_5H_5Mo(CO)[(C_6H_5)_3P]_2Cl$, CH_3CN and $AlCl_3$. All cations were eventually characterized as hexafluorophosphate salts.

REFERENCES

1 P. M. TREICHEL AND G. P. WERBER, *J. Organometal. Chem.*, 7 (1967) 157.
2 T. A. MANUEL, in F. G. A. STONE AND R. WEST (Eds.), *Advances in Organometallic Chemistry*, Vol. 3, Academic Press, New York, 1966, p. 181.
3 R. B. KING, *Inorg. Chem.*, 2 (1963) 936.
4 E. O. FISCHER AND E. MOSER, *J. Organometal. Chem.*, 5 (1966) 63.
5 E. O. FISCHER AND E. MOSER, *J. Organometal. Chem.*, 2 (1964) 230.
6 E. O. FISCHER, K. FICHTEL AND K. OFELE, *Chem. Ber.*, 95 (1962) 3172.
7 E. O. FISCHER AND K. FICHTEL, *Chem. Ber.*, 94 (1961) 1200.
8 C. E. COFFEY, *J. Inorg. Nucl. Chem.*, 25 (1963) 179.
9 M. L. H. GREEN AND A. N. STEAR, *J. Organometal. Chem.*, 1 (1964) 230.
10 R. B. KING, *Organometallic Syntheses*, Vol 1, Academic Press, New York, 1965, p. 109.
11 T. S. PIPER AND G. WILKINSON, *J. Inorg. Nucl. Chem.*, 3 (1956) 104.