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REACTIONS OF ARENETRICARBONYL–GROUP VIB METALS WITH HALIDE AND PSEUDOHALIDE IONS

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SUMMARY

A variety of compounds of general formula $(R_4N)_3[(CO)_3MX_3M(CO)_3]$ (M = Cr, Mo, W; X = F, Cl, Br, I, OH, SCN, N_3, OC_2H_5) were prepared from AreneM$(CO)_3$ and tetraalkylammonium halide. A few compounds were prepared with two-member bridges with the formula $(R_4N)_2[(CO)_3MX_2M(CO)_3]$. These very rapid reactions of AreneM$(CO)_3$ with free halide and pseudohalide ions demonstrate the strong Lewis acid properties of AreneM$(CO)_3$, and provide support for the contention that AreneM$(CO)_3$ serve as effective catalysts in Friedel–Crafts reactions by promoting ionic-type reactions.

INTRODUCTION

In a recent paper[1] we reported that AreneM$(CO)_3$ (M = Cr, Mo, W) is an effective homogeneous catalyst in promoting Friedel–Crafts type reactions. Our evidence indicates that AreneM$(CO)_3$ is capable of generating carbonium ions from organic halides; this activity suggests that AreneM$(CO)_3$ has a strong affinity for halide ions. In order to test this hypothesis and at the same time gather information to aid us in understanding the mechanistic aspects of carbonium ion generation, we have allowed various AreneM$(CO)_3$ compounds to react with free halide and pseudohalide ions. This paper reports the results of these reactions.

EXPERIMENTAL

Starting materials

Chromium, molybdenum and tungsten hexacarbonyls were used without further purification upon receipt from various suppliers, as were the tetramethylammonium halides and tetraphenylarsonium chloride. All solvents were deoxygenated by purging with nitrogen.

The arenemetal tricarbonyls were prepared according to the method described by Nichols and Whiting[2].

Hexamethylethylenediammonium diiodide and octamethylbis(trimethylene)-

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triammonium triiodide were prepared according to the method reported by Walker[3]. For the preparation of the former compound, an excess of CH_3I in ethanol was added to a cooled (0°) ethanol solution of tetramethylethylenediamine (Eastman) with stirring. The reaction mixture was then refluxed for 2 h. The resulting precipitate was collected by filtration and washed with ethanol and ether and air dried. The yield of hexamethylethylenediammonium diiodide was essentially quantitative, m.p. 287°.

Octamethylbis(trimethylene)triammonium triiodide was prepared in a manner similar to that described above from methylation of pentamethylbis(trimethylene)-triamine, obtained from methylation of bis(3-aminopropyl)amine according to the method of Icke and Wisegarver[4]. The yield was essentially quantitative, m.p. 291–292°.

The ammonium iodides thus prepared were converted to di- and trihydroxides by ion exchange on a column of Ionac AGA-542 resin. The hydroxides were then converted to their respective chlorides by neutralization with HCl.

Tetramethylammonium thiocyanate was prepared by metathesis from $(CH_3)_4$-NCl with NaSCN in methanol and purified by three recrystallizations from water/ethanol. (Found: C, 45.00; H, 9.21; N, 21.09; S, 24.17. $C_5H_{12}N_2S$ calcd.: C, 45.43; H, 9.15; N, 21.18; S, 24.25%.)

Tetraethylammonium azide was prepared *in situ* from equimolar amounts of $(C_2H_5)_4NClO_4$ and NaN_3.

Instrumental methods

Infrared spectra were recorded as Nujol mulls between KBr discs on a Perkin–Elmer Model 337 Grating Infrared Spectrophotometer. Conductivity measurements were carried out on a Serfass Model RCM 15 conductivity bridge using a Yellow Springs 3402 dipping cell. Solutions for conductivity measurements were prepared from deionized, distilled, and deoxygenated water; the measurements were performed under a nitrogen atmosphere.

Preparation of the complexes

All operations were carried out under an atmosphere of nitrogen.

A. Preparation of $(R_4N)_3[(CO)_3MX_3M(CO)_3]$ (R = CH_3 or C_2H_5 as indicated in Table 1. M = Mo or W except as noted below. X = F, Cl, Br, I, OH, SCN, N_3). The following account describes the preparation of $[(CH_3)_4N]_3[(CO)_3MoCl_3Mo(CO)_3]$; all other compounds in this series were prepared similarly with exceptions noted at the end of the account of the preparation.

Toluenemolybdenum tricarbonyl (0.55 g, 2.0 mmole), dissolved in 70 ml of ethanol, was treated by rapid addition of 60 ml of an ethanol solution containing 0.66 g (6.0 mmole) of tetramethylammonium chloride, with stirring, at room temperature. The bright yellow precipitate which formed immediately was filtered, washed with 4 x 25 ml portions of ethanol followed by 3 x 25 ml portions of pentane, and dried *in vacuo*. The yield was nearly quantitative.

Exceptions. When the starting material was mesitylenemolybdenum tricarbonyl or arenetungsten tricarbonyl, the reaction mixture required heating (40–60°) for 2 to 4 h to ensure complete reaction. No reaction was observed for $AreneCr(CO)_3$ with R_4NX (X = F, Cl, Br, OH), or where the metal was tungsten and X = SCN and N_3.

B. Preparation of $[(CH_3)_4N]_3[(CO)_3MX_3M(CO)_3]$ *from* $M(CO)_6$ (M = Cr, Mo,

TABLE 1

ELEMENTAL ANALYSIS AND CONDUCTIVITY

R	*X*	*M*	*Found (calcd.) (%)*					*Ω (ohm^{-1})*	*Color*
			C	*H*	*N*	*X*	*M*		
A. $[R_4N]_3[(CO)_3MX_3M(CO)_3]$ *prepared from* $AreneM(CO)_3$									
CH_3	Cl	Mo	31.32	5.31	6.07	15.09	28.00	366	Yellow
			(31.39)	(5.27)	(6.09)	(15.44)	(27.85)		
CH_3	Br	Mo	26.53	4.71	5.28	30.07	23.47		Yellow
			(26.29)	(4.41)	(5.11)	(29.16)	(23.34)		
C_2H_5	I	Mo	31.77	5.10	3.81	33.75	17.03		Yellow-orange
			(31.85)	(5.34)	(3.71)	(33.65)	(16.96)		
CH_3	Cl	W	24.71	4.09	4.81	12.27	42.31	392	Yellow
			(25.00)	(4.19)	(4.86)	(12.30)	(42.53)		
CH_3	Br	W	21.47	3.66	4.18	24.06	37.70		Yellow
			(21.66)	(3.64)	(4.21)	(24.02)	(36.85)		
CH_3	SCN	Mo	32.27	5.10	11.22	12.01[a]	25.77	415	Yellow
			(33.34)	(4.78)	(11.10)	(12.71)	(25.36)		
C_2H_5	N_3	Mo	40.96	7.15	19.75			388	Yellow
			(41.09)	(6.91)	(19.16)				
B. $(R_4N)_3[(CO)_3MX_3M(CO)_3]$ *prepared from* $M(CO)_6$									
CH_3	Cl	Mo	31.41	5.29	6.29	15.77			Yellow
			(31.39)	(5.27)	(6.09)	(15.44)			
CH_3	Br	Mo	26.35	4.85	5.44	29.55			Yellow
			(26.29)	(4.41)	(5.11)	(29.16)			
K	OC_2H_5	Mo	23.51	2.73			31.45		
			(23.52)	(2.45)			(31.37)		
CH_3	Cl	W	25.13	4.44	7.46	11.28			Yellow
			(25.00)	(4.19)	(4.86)	(12.30)			
C. $[(CH_3)_3NCH_2CH_2N(CH_3)_3]_3[(CO)_3MX_3M(CO)_3]_2$ *prepared from* $AreneM(CO)_3$									
	Cl	Mo	31.48	5.17	6.24	15.62			Yellow
			(31.52)	(4.86)	(6.12)	(15.51)			
	N_3	Mo	30.69	4.83	22.69			649	Yellow
			(30.65)	(4.72)	(23.82)				
$[(CH_3)_3N(CH_2)_3N(CH_3)_2(CH_2)_3N(CH_3)_3][(CO)_3MX_3M(CO)_3]$									
	Cl	Mo	32.15	5.41	5.40	13.78		446	Yellow
			(33.69)	(5.09)	(5.89)	(14.92)			
D. $(R_4N)_2[(CO)_3MX_2M(CO)_3]$ *prepared from* $AreneM(CO)_3$									
C_2H_5	I	Mo	30.25	4.78	3.25	29.33	22.05		Orange
			(30.22)	(4.58)	(3.21)	(29.05)	(21.95)		
C_6H_5[b]	Cl	Mo	54.07	3.84		6.09	15.92		Yellow
			(54.16)	(3.37)		(5.92)	(16.02)		

[a] X=sulfur; [b] N=As.

W; X=F, Cl, Br). The product was obtained by filtration after refluxing an ethanol solution containing 2 mmole of $M(CO)_6$ and 6–8 mmole of tetramethylammonium halide for 6 to 12 h. The precipitate was washed with copious amounts of ethanol, followed by several washings with benzene, and dried *in vacuo*. Also obtained from this method of preparation was the compound $K_3[(CO)_3Mo(OC_2H_5)_3Mo(CO)_3]$.

C. Preparations of $[(CH_3)_3NCH_2CH_2N(CH_3)_3]_3[(CO)_3MoX_3Mo(CO)_3]_2$ *and* $[(CH_3)_3N(CH_2)_3N(CH_3)_2(CH_2)_3N(CH_3)_3][(CO)_3MoX_3Mo(CO)_3]$. These compounds were prepared in a manner similar to that described in *B* except that a slight excess of $AreneMo(CO)_3$ was used to ensure complete reaction of the quaternary ammonium salts.

D. Preparations of the doubly-bridged complexes. The preparation of $[(CH_3)_4N]_2[(CO)_3Mo(OH)_2Mo(CO)_3]$ was achieved in a manner similar to that described under *A* from tetramethylammonium hydroxide and toluenemolybdenum tricarbonyl. $[(CH_3)_4N]_2[(CO)_3Cr(OH)_2Cr(CO)_3]$ was prepared as described under *B* from a refluxing ethanol solution of $Cr(CO)_6$ and $(CH_3)_4NOH$. The preparation of $[(C_2H_5)_4N]_2[(CO)_3MoI_2Mo(CO)_3]$ was effected by the method described under *A*, except that equimolar amounts of $(C_2H_5)_4NI$ and $TolMo(CO)_3$ (Tol=toluene) were employed. The preparation of $[(C_6H_5)_4As]_2[(CO)_3MoCl_2Mo(CO)_3]$ was carried out by treating $TolMo(CO)_3$ (0.675 g, 2.5 mmole) with $(C_6H_5)_4AsCl$ (1.84 g, 4.4 mmole) in 125 ml of ethanol. After the solution was stirred for 3 h at room temperature, 300 ml of pentane was added and the resulting precipitate was filtered from the solution, washed with pentane and dried *in vacuo*.

RESULTS AND DISCUSSION

Elemental analyses, conductivities and colors of the compounds prepared in this work are presented in Table 1.

Properties of the complexes

The complexes prepared in this work are generally unstable upon exposure to air. The triply-bridged complexes decompose more or less rapidly in the presence of oxygen, and aqueous solutions of the complexes are particularly susceptible to oxidation. The double-bridged complexes decompose very rapidly on exposure to air; in fact, they are nearly pyrophoric in the solid state.

Both the doubly- and triply-bridged compounds are soluble in water and DMSO, but are generally insoluble in most organic solvents. Aqueous solutions of the complexes are relatively stable if prepared and handled under an inert atmosphere. Not included in Table 1 are the following compounds: $[(CH_3)_4N]_3[(CO)MX_3M(CO)_3]$ (for M=Cr; X=F, Cl; for M=Mo; X=F; for M=W; X=F, OH) and $[(CH_3)_4N]_2[(CO)_3M(OH)_2M(CO)_3]$ (M=Cr, Mo). These compounds are particularly unstable and satisfactory elemental analyses were not obtained. However, we were able to obtain satisfactory CO evolution analyses, upon decomposition with I_2 in pyridine, on the freshly prepared fluoride complexes of $[(CH_3)_4N]_3[M_2(CO)_6F_3]$: for M=Cr; CO found 30.67, (calcd. 30.46%); for M=Mo: CO found 25.88, (calcd. 26.78%); for M=W: CO found 20.36, (calcd. 20.61%).

Characterization of the complexes

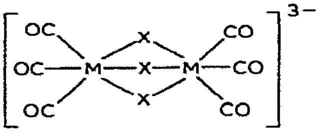
Structural information was deduced from elemental analyses, infrared spectra and conductivity measurements. In the case of the less stable complexes where elemental analyses were poor, the compounds were classified as to structural type by infrared and conductivity data; the differentiation of double- and triply-bridged anions is relatively clear on this basis.

In general, all the triply-bridged complexes exhibit two main bands in the CO stretching region, ca. 1880 (±10) and 1740 (±10) cm^{-1}. In addition, the thiocyanate and azide derivatives show bands in the 2000 cm^{-1} region indicative of these ligands. The doubly-bridged anions exhibit three main bands in the CO stretching region, ca. 1895, 1860 and 1700 cm^{-1}; the lowest frequency band is generally broad. In the spectra of some of both types of compounds, poorly defined shoulders appear on the main bands.

Also providing supporting evidence for the bridging nature of the anions is a comparison of infrared data for the thiocyanate and azide complexes in this work with those of other compounds where the anions are known to bridge. For example, in the anion $[(CO)_3Mo(SCN)_3Mo(CO)_3]^{3-}$, the CN stretching frequencies are found at 2132 and 2096 cm^{-1}. The higher value compares favorably with that of 2160 cm^{-1} for[5] $[Mn_2(CO)_6(CNS)_4]^{2-}$ and also with those of 2143 and 2138 cm^{-1}, respectively, found by Ruff[6] for the anions $[M_2(CO)_2(CNS)]^-$ (M=Cr, W). The lower value in this work is not assignable to a bridging thiocyanate where both the S and N atoms are involved in bonding, in light of existing data. We cannot be sure of whether the value of 2096 cm^{-1} is indicative of a terminal thiocyanate or bridging by a different mode of bonding at this time.

Bridging azides in some carbonyl complexes of Mn and Re have shown $\nu(N_3)$ values in the 2058–2088 cm^{-1} region[7], while $\nu(N_3)$ for the anion $[(CO)_3Mo(N_3)_3Mo(CO)_3]^{3-}$ occurs at 2060 cm^{-1}.

We believe the structure of the triply-bridged anion to be:

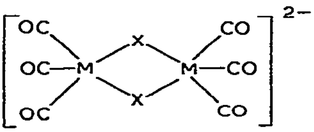


This structure is indicated primarily from conductivity measurements. The molar conductivity values in aqueous solution for these complexes, with R_4N^+ as the cation, are in the 360–420 ohm^{-1} range, indicative of 4 ions per formula. This compares favorably with other 3/1 electrolytes, such as $[Pt(NH_3)_5Cl]Cl_3$, which has a molar conductance value of 404 ohm^{-1} (see, for example ref. 8). An alternative structure for these compounds could be a tetrameric rather than a dimeric structure, where the metal atoms might be arranged at the corners of a tetrahedron with the six halide ions in bridging positions on the edges. The result of this arrangement would be a 6/1 electrolyte, and conductivity values would certainly be expected to be substantially higher than those found for the compounds, although we were not able to find a standard for comparison. Nonetheless, we prepared some quaternary ammonium cations of charges +2 and +3. In the case of $[(CH_3)_3N(CH_2)_2N(CH_3)_3]_3[(CO)_3Mo(N_3)_3Mo(CO)_3]_2$ the molar conductivity value was found to be 649 ohm^{-1}. This compares favorably with the standard $Ca_3[Fe(CN)_6]_2$, which is known to contain 5 ions per formula weight and shows a molar conductivity[9] of 680 ohm^{-1}. If the anion were tetrameric, the compound produced would be of the formula $[Cat^{2+}]_3[An^{6-}]$, and, while we were not able to locate a standard reference, should show significantly higher values than those found.

A comparison of the conductivity values of $[(CH_3)_3N(CH_2)_3N(CH_3)_2(CH_2)_3N(CH_3)_3][(CO)_3MX_3M(CO)_3]$ with a standard ionic compound $[CoEn_3][Fe(CN)_6]$, which is of the general formula $[Cat^{3+}][An^{3-}]$, reveals that they are similar ionic types. For example, the former compound exhibits a conductivity value of 446 ohm^{-1} while a solution of the latter shows a value[10] of 462 ohm^{-1}. Once again, if the anion were tetrameric in nature, a compound of the formula $[Cat^{3+}]_2[An^{6-}]$ would be obtained, and conductivity values would be expected to occur in a substantially higher range than that found. Other conductivity values may be found in Table 1.

The proposed triply-bridged structure is not without precedent. A similar structure has been proposed for some π-allyl carbonyl compounds of Mo with bridging Cl and Br ions[11]. In addition, a triply-bridged azide complex is also known[7], as are triply-bridged hydride[12], alkoxide[12,13], and hydroxide[13] compounds.

In certain instances, doubly-bridged compounds are formed. The following structure is proposed for the anions:



The major evidence for this structure once again is based on conductivity measurements. The molar conductivity values found in the 200–250 ohm^{-1} range compare favorably with standard 2/1 electrolytes, *viz.*, $[Pt(NH_3)_4Cl_2]Cl_2$, K_2PtCl_6, and $[Co(NH_3)_5NO_2]Cl_2$, which show values of 228, 256, and 246 ohm^{-1}, respectively.

It is not clear why the doubly-bridged complexes are formed in a few cases; however, the extremely unstable nature of these compounds toward oxygen is apparent since the metals are electron deficient with respect to the effective atomic number rule.

It is interesting to note the novel compounds prepared in this work, namely, the fluoride, hydroxide, azide, and ethoxide derivatives. Metal carbonyl fluoride[14,15], hydroxide[13,16,17], and alkoxide[12,13] complexes are particularly rare; bridging azide ligands are of interest because of various possibilities in modes of bonding between two metals.

The fluoride and hydroxide complexes, as noted previously, are markedly unstable. We have observed decomposition from the yellow freshly prepared compound to a very dark decomposition product in a freezer over a period of two days. It is not surprising, therefore, that unsatisfactory analyses were obtained; however, in light of the CO studies on freshly prepared complexes and infrared studies (*vide supra*, we feel that, indeed, these complexes are formed.

The point of this research is made that $AreneM(CO)_3$ has strong Lewis acid properties and the rapid reaction with anions of many types provides support for our proposal that the catalysts promote ionic-type reactions[1]. Noting the reaction with fluoride ion, we carried out an alkylation of toluene with cyclohexyl fluoride, similar to that described in ref. 1. After the reaction mixture was refluxed for 6 h, a 77% yield of cyclohexyl toluene was obtained. Furthermore, our catalyst promoted 100% polymerization of benzyl fluoride to polybenzyl, which also was reported to occur for benzyl chloride[1].

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