reagent with Me_2PCl, with **6** constituting about 85–90% of the mixture. This ratio was maintained on sulfurization to form **17** and **19**, and methylation to **22** and **24**. Fractional distillation of the phosphonous dichlorides also provided a sample enriched to about 80% in the cis isomer (**11**) and this was used to form the entire series of cis compounds by conventional reactions.[5] For the 4-methylcyclohexyl series, a trans-rich (80–90%) tertiary phosphine mixture (**5** and **7**) resulted from the Grignard reaction, and this led to sulfide (**16** and **18**) and salt (**21** and **23**) mixtures similarly enriched. Data for the *cis*-4-methylcyclohexyl series were obtained on mixtures of nearly 1:1 cis–trans composition.

Registry No.—1, 822-68-4; **2**, 58359-91-4; **3**, 58359-90-3; **4**, 58359-87-8; **5**, 58403-25-1; **6**, 58359-93-6; **7**, 55615-34-4; **8**, 58359-92-5; **9**, 2844-89-5; **10**, 58359-95-8; **11**, 58359-94-7; **12**, 16195-98-5; **13**, 58359-97-0; **14**, 58359-96-9; **15**, 58359-88-9; **16**, 58360-05-7; **17**, 58359-99-2; **18**, 58360-04-6; **19**, 58359-98-1; **20**, 58359-89-0; **21**, 58360-07-9; **22**, 58448-99-0; **23**, 58360-06-8; **24**, 58449-00-6.

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Organometallic Chemistry. 9.[1] Carbon-13 Nuclear Magnetic Resonance Study of the Cumylchromium Tricarbonyl and of Cycloheptatrienylmolybdenum (-chromium, and -tungsten) Tricarbonyl Cations

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The cumylchromium tricarbonyl cation was prepared under long-lived ion conditions, and studied by NMR (^1H and ^{13}C) spectroscopy. For comparison, the carbon-13 NMR parameters of three cycloheptatrienyl-$M(CO)_3$ cations (M = Mo, Cr, and W) were also determined and are reported. Based on the ^{13}C NMR studies the origin of the unusual stabilization of the cumylchromium tricarbonyl ion is discussed. The σ^+ substituent constant for the $Cr(CO)_3$ group and the fraction of the unit positive charge transmitted into the $M(CO)_3$ groups were qualitatively estimated.

The substituent effect of the metal tricarbonyl moiety in metal–arene complexes is of substantial interest. There is considerable evidence to show that π-complexed $Cr(CO)_3$ group exerts a net electron-withdrawing effect from the aromatic ring.[3] The deprivation of π-electron density on the aromatic ligand upon complexation with the $Cr(CO)_3$ group also appears to attenuate the substituent effect of other aryl substituents. On the other hand, the electron-releasing effect of the $Cr(CO)_3$ group has been demonstrated by the rate enhancement of solvolysis of tricarbonylchromium complexes of benzyl,[4,5] cumyl,[5] and 2-benzonorbornenyl[6] derivatives, and the increase of the $pK_R{}^+$ value for the benzylchromium tricarbonyl cation.[7] They were explained by the increase of stability of the intermediate cation with the attachment of the $Cr(CO)_3$ moiety. Previous attempts at the isolation of benzyl-, diphenylmethyl-, and triphenylmethylchromium tricarbonyl cations from the corresponding alcohols failed.[4] Upon treatment with $HClO_4$ or HBF_4 in Ac_2O, the alcohols gave only rapid decomposition. We would like to report now the preparation of the cumylchromium tricarbonyl cation **1**, the first chromium tricarbonyl complexed arylalkyl cation observed under long-lived conditions, and its ^1H and ^{13}C NMR spectroscopic study. The results provide evidence for the unusual stabilization of **1** through charge delocalization into the $Cr(CO)_3$ group. For comparison, we also determined the ^{13}C NMR spectroscopic parameters of three known cycloheptatrienylium-$M(CO)_3$ cations **2** (M = Mo, Cr, and W). Cations **2** represent a cyclic six π electron aromatic system attached to a metal tricarbonyl group, whereas **1** represents a similar six π electron system substituted by an electron-deficient exocyclic carbenium ion grouping.

Results and Discussion

A dark-green solution of the cumylchromium tricarbonyl cation **1** was obtained upon treatment of a solution of the chromium tricarbonyl complex of cumyl alcohol with fluorosulfuric acid in SO_2 at −80 °C under dry nitrogen. The carbon-13 spectrum of **1** is shown in Figure 1 and the ^1H and ^{13}C NMR parameters are summarized in Tables I and II, respectively, together with the data of the corresponding ions

Table I. ^{1}H NMR Parameters of the Cumylchromium Tricarbonyl Cation and Related Cumyl Cations

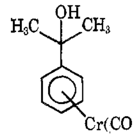
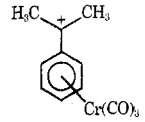
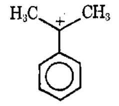
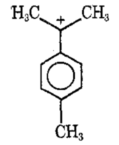
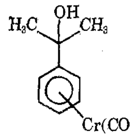
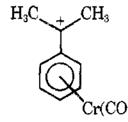
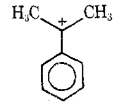
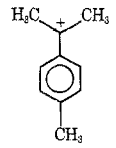
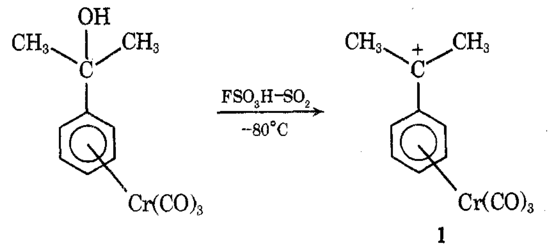
Registry no.	Compd	Ring protons	CH_3	OH
52409-32-2		5.37 (3 H), m 5.67 (2 H), m	1.58 (6 H), s	2.00 (1 H), s
58464-00-9		5.97 (3 H), m 5.32 (2 H), m	1.73 (6 H), s	
16804-70-9		8.73 (2 H) 7.82 (2 H) 8.42 (1 H)	3.48 (6 H)	
20605-66-7		8.72 (2 H) 7.40 (2 H)	3.12 (6 H)	

Table II. ^{13}C NMR Parameters of Cumylchromium Tricarbonyl Cation and Related Cumyl Cations

Compd	C_α	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	CH_3	CO
	71.42	121.92	92.32	94.57	92.32	31.72	234.19
	170.92	101.66	99.49	120.67	96.72	24.74	228.39
	254.3	140.0	142.4	133.3	155.9	34.90	
	242.79	137.69	141.52	133.51	174.43	30.90	

and precursors. Noteworthy is that the benzylic carbon becomes deshielded upon ionization of the alcohol to **1**, but the shift is smaller compared to that observed in the corresponding parent, uncomplexed system. The significant shielding of the electron-deficient benzylic carbon in **1**, compared to that of the uncomplexed cumyl cation, indicates the unusual stabilization of the cumyl cation upon complexation and the extensive delocalization of charge through the whole complexed ion. However, the electron-deficient exocyclic carbon in **1** is more deshielded compared to that observed in the α-ferrocenylcarbinyl cation.[8] The carbon chemical shifts of **1** are overall shielded by 312.3 ppm compared to the uncomplexed cumyl cation. From this shielding about 200 ppm is attributed to the change of the bonding nature upon complexation,[3] and the remaining 100 ppm corresponds to the transmission of ⅓ of the unit positive charge into the $Cr(CO)_3$ group, if the effects other than the development of charge are small. Recent carbon-13 spectroscopic study of benzylic carbocations showed that the carbon shifts reflected the trend of positive charge density distribution, correlating with the ability of substituents to delocalize positive charge and indicating the stability of ions.[9] Utilizing the observed Hammett type relationship between carbenium carbon shifts of substituted cumyl cations and Brown's σ^+ substituent constants,[10] a σ^+ value of −1.8 is estimated for the $Cr(CO)_3$ group (Figure 2).[9] Unlike the complexed benzyl and benzhydryl chlorides,[4] recent kinetic study on the rate of solvolysis of cumyl chloride–chromium tricarbonyl[5] indicated that the $Cr(CO)_3$ group is capable of enhancing the rate only by a factor of 28 and that it is comparative to a *p*-methyl group.[10] Since observed ΔH and ΔS values are much different from those of the uncomplexed system, it is proposed that a different mechanism is involved in the solvolysis of the chromium tricarbonyl complexed cumyl chloride.



1

Ions **2** were conveniently prepared by hydride abstraction from the corresponding cycloheptatriene–$M(CO)_3$ complexes

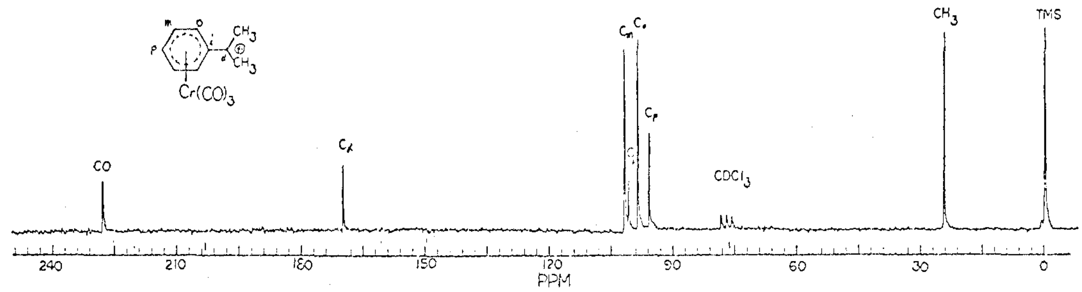


Figure 1. Carbon-13 spectrum of cumylchromium tricarbonyl cation in SO_2 at −70 °C.

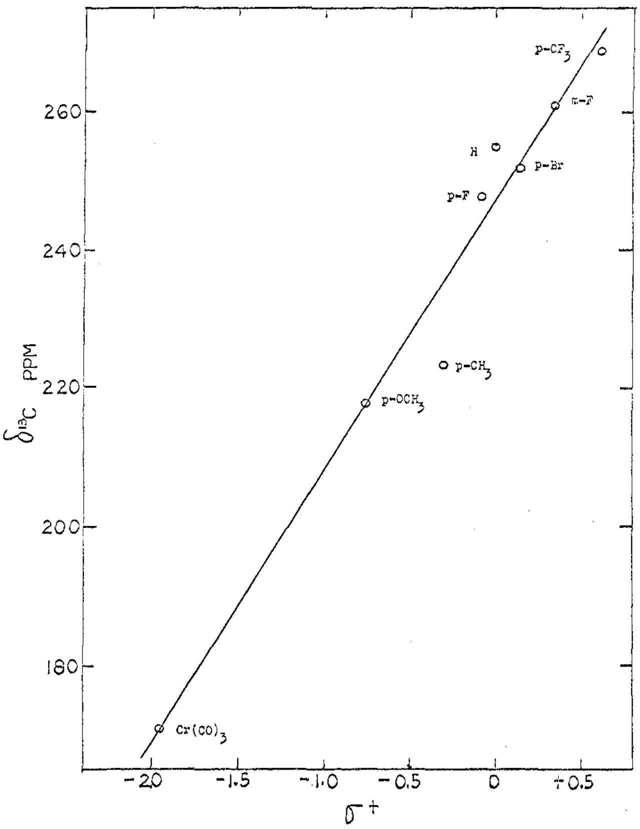
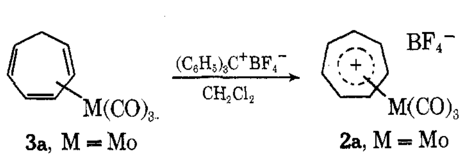


Figure 2. Correlation of carbenium carbon ^{13}C NMR chemical shifts to Brown's σ^+ substituent constants for substituted cumyl cations.



3a, M = Mo
b, M = Cr
c, M = W

2a, M = Mo
b, M = Cr
c, M = W

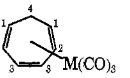
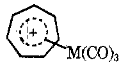
3 with triphenylcarbenium fluoroborate.[11] The ^{13}C NMR parameters of ions **2** and compounds **3** are summarized in Table III. Upon hydride abstraction, all ring carbons become equivalent as a single resonance and is deshielded. However, the deshielding effect is smaller compared to that observed for the corresponding uncomplexed tropylium ion indicating that the $M(CO)_3$ group also stabilizes the ions **2** by delocalizing charge. The almost identical deshieldings observed when compounds **3** are converted into **2** suggest that the molybdenum, chromium, and tungsten tricarbonyl groups have nearly equivalent stabilizing effects. The present data are also consistent with the previously determined $pK_R{}^+$ values of ions **2**, which are almost identical, and are larger than that for the tropylium ion.[12] The chemical shifts of uncomplexed cycloheptatriene are overall deshielded by 284 ppm upon hydride abstraction, corresponding to development of unit positive charge. The difference of overall chemical shifts between **2b** and **3b** is 188 ppm. The deshielding is 96 ppm less than that of the uncomplexed, parent system and corresponds to ⅓ of the unit positive charge being transmitted into the $Cr(CO)_3$ group. It is interesting to compare this observation with cation **1**, where it is also estimated that ⅓ of the unit positive charge is transmitted. In the same manner, it is estimated that approximately ½ of the unit positive charge is transmitted into the $M(CO)_3$ groups in **2c** and **2a.**

The increase in shielding of the carbonyl resonance in **1** with respect to that of the corresponding alcohol and arenechromium tricarbonyls,[3] and **2a** with respect to that of **3a**, is consistent with the decrease of the electron density on the metal owing to transmission of charge to stabilize the cationic ligand.[13] It is also consistent with the decrease in the metal–carbonyl π back-donation with increasing carbonyl stretching frequencies.[11,12] Furthermore, the observation of a single resonance for the carbonyl carbons in **1** and **2a** points out the low rotational barrier of the $M(CO)_3$ group relative to the cationic ligand.

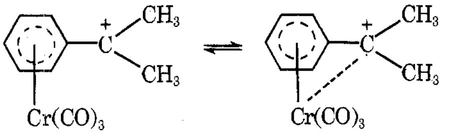
The bonding of the transition metal π complexes with olefinic ligands has generally been considered to be composed of a σ forward donation arising from an overlap of the filled bonding π orbital of the ligand with vacant orbitals of the metal and a π back-donation from an overlap of a filled d orbital of the metal with the antibonding π orbital of the ligand.[14] The general significance of π back-donation is well known. For the present electron-deficient system, the back-donation is of particular significance, for it transmits the electronic charge density into the cationic ligand to counterbalance the developed positive charge. It is expected that the formation of a nonbonding orbital in the cumyl cation[15] upon ionization depresses the energy level of the lowest unoccupied orbital and facilitates back-donation,[15] whereas in the case of the cycloheptatrienylium ion no nonbonding orbital is formed. Consequently the $Cr(CO)_3$ group has less stabilizing effect on the cycloheptatrienylium ion than on the cumyl cation, as also is indicated by the previous $pK_R{}^+$ measurements.[7] It is of interest that the ring carbons in **1** which are not at the nodal plane in the nonbonding orbital are more shielded, owing at least in part to the increase of back-donation between these carbons and the metal atom. However, because of the qualitative nature of estimating effects on charge deshielding, the present study cannot claim to have detected any transmission of excess charge into the $Cr(CO)_3$ group in **1** due to more favorable π back-donation, by comparison with **2b.**

In addition to the above-mentioned stabilization through back-donation with the interaction of the metal atom with the whole π-electron system of the cationic ligand,[16] the origin[17] of the unusual stabilization of transition metal π complexes containing an exocyclic electron-deficient ligand has been proposed to be due to direct metal participation (**4**),[18] σ–π conjugation (vertical stabilization, **5**),[19] or π–π type overlap.[20] In both chromium tricarbonyl complexed and uncomplexed

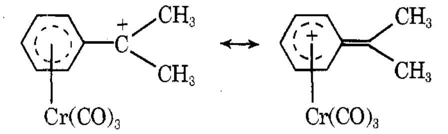
Table III. Carbon-13 Parameters of Cycloheptatriene, Tropylium Ion, and Their π Complexes with Molybdenum, Chromium, and Tungsten Tricarbonyls[a]

Metal carbonyl	Registry no.						Registry no.		
		C_1	C_2	C_3	C_4	CO		CH	CO
		123.3 (161.1)	129.8 (154)	134.1 (156)	28.8 (131)	*b*		155.33 (168.6)	
$Cr(CO)_3$	12125-72-3	58.15	102.27	100.22	24.17	a 241.34[c,d] b 230.14	12170-19-3	104.71 (179.3)	*e*
$Mo(CO)_3$	12125-77-8	62.36	104.43	99.68	27.08	a 229.17[c,d] b 217.93	12170-21-7	100.0 (176.9)	206.29
$W(CO)_3$	12128-81-3	52.3	101.7	94.2	28.7	211.6 (av)[d]	12083-17-9	96.62 (179.9)	*e*

[a] All chemical shifts (ppm) are referred to the external Me_4Si capillary, and coupling constants (Hz) are given in parentheses. [b] H. Spiesecke and W. G. Schneider, *Tetrahedron Lett.*, 468 (1961); H. Gunther, *Z. Naturforsch.*, 206, 948 (1965). [c] C. G. Kreiter and M. Lang, *J. Organomet. Chem.*, 55, C27 (1973). [d] B. E. Mann, *Chem. Commun.*, 926 (1971). [e] Several attempts were made; however, no resonance was observed for the carbonyl carbons.



4



5

monosubstituted benzene derivatives the ortho and para carbons are generally sensitive to the effect of a ring substituent, whereas the meta carbons are almost unaffected.[3] However, the situation is reversed in **1**. As in the case of arenium–iron tricarbonyl cations,[21] the meta carbons are affected most and become most deshielded. The observation of the reversed deshielding sequence in 1 rules out direct metal participation and π–π type overlap. Although an excellent agreement of the related chemical shifts has been reported between free and chromium tricarbonyl complexed arenes,[3] it cannot be extrapolated to **1**. It indicates that substantial perturbation takes place in the transmission of resonance substituent effects in 1 and rules out the σ–π conjugation. In addition, if 1 would be stabilized by σ–π conjugation, C_i should be observed at a much lower field based on the structures represented as **5**.

Finally, we would like to point out that our estimation of the σ^+ substituent constant of the $Cr(CO)_3$ group and the amount of fractional positive charge transmitted into the metal ligand is clearly qualitative, with the assumption that the shieldings are only moderately affected by the change of bonding nature upon formation of the cations. ^{13}C NMR shift differences clearly cannot be equated with charge delocalization, but qualitatively seem to show their trend.[22] This is considered to be the case also for the cations of transition metal π complexes, although no satisfactory theory is yet available for the shielding effects in these complexes.[23] Furthermore, we also would like to point out that the charge transmission into the $M(CO)_3$ group could be a major contributor to the unusual stabilization. However, it is not the sole factor to be considered and the stabilization is dependent on the charge delocalization of the whole molecule.

Experimental Section

Molybdenum, chromium, and tungsten carbonyls were obtained from Strem Chemicals, Inc. Cycloheptatriene and cumyl alcohol were purchased from the Aldrich Chemical Co. Cycloheptatrienyl-$M(CO)_3$ ions (M = Mo, Cr, and W) were conveniently prepared, as reported, by hydride abstraction from the corresponding cycloheptatriene-$M(CO)_3$ complexes with triphenylcarbenium tetrafluoroborate.[11] Cumyl alcohol–chromium tricarbonyl was prepared as reported.[4] A dark green solution of the cumylchromium tricarbonyl cation was obtained upon treatment of the alcohol in cold $CDCl_3$ with fluorosulfuric acid in SO_2 at −80°, under dry nitrogen. The cation is stable indefinitely up to −30 °C.

The ^1H NMR spectra were obtained on a Varian A56/60A spectrometer with a capillary of Me_4Si as external reference. FT ^{13}C NMR spectra were obtained on a Varian XL-100 spectrometer, using fluorobenzene as external lock. All chemical shifts are referred to the external Me_4Si (5% enriched capillary).

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