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PREPARATION AND CHARACTERIZATION OF SOME TRIPHENYLMETHYL COMPOUNDS OF CHROMIUM

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ABSTRACT

The preparation of the previously unreported compounds, $NaCr(CO)_5C(C_6H_5)_3$, $NaCr(CO)_3C(C_6H_5)_3$, and $Cr(C(C_6H_5)_3)_2$, is described. The success of the novel preparation of $Cr(C(C_6H_5)_3)_2$ from the carbonyl compounds apparently results from the peculiar characteristics of the triphenylmethyl ligand.

From analysis of the carbonyl stretching frequencies of $NaCr(CO)_5C(C_6H_5)_3$ and $NaCr(CO)_3C(C_6H_5)_3$, the π-acceptor strength of the triphenylmethyl ligand is shown to be greater in the tricarbonyl compound. Therefore, σ bonding is proposed for the triphenylmethyl group in the pentacarbonyl compound and π-allylic bonding is proposed for this group in the tricarbonyl compound and in $Cr(C(C_6H_5)_3)_2$. The compatiblity of the observed properties of the compounds with these bonding models and with several alternative models is discussed.

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INTRODUCTION

The historical development of the organometallic chemistry of the transition metals entails an interesting illustration of the manner in which theoretical and synthetic advances follow and stimulate each other. The subject is presently at a point in its development where recent advances in synthesis are stimulating theoretical efforts. A brief historical review will serve to establish the role of the present investigation in this evolutionary process.

Very early organometallic chemistry was dominated by the Grignard reagent, ethyl ether solutions of organomagnesium halides. The first preparations of organometallic compounds of the transition metals resulted from reaction, attempted largely without theoretical basis, of various Grignard reagents with metal halides. Included in this class of experiments is the first preparation of an organochromium compound, $(C_6H_5)_5CrBr$, reported by Hein in 1919 (1) to result from the action of phenyl Grignard reagent on anhydrous chromium (III) chloride. In the

following three decades, Hein synthesized a very large number of other polyarylchromium compounds by analogous methods (2-22).

Unsupported by structural data, Klemm and Neuber (23) and Hein (24) suggested that these are compounds containing conventional metal-to-carbon sigma (σ) bonds; that is, compounds in which the carbon-metal bond arises from donation of electrons from a single carbon atom in the organic group to the metal atom. Definitive structural investigations were later performed by Fischer (25-29) and by Zeiss and Tsutsui (30) which demonstrated that these compounds are aromatic complexes containing no σ bonds between metal and carbon. In aromatic complexes, π electrons are donated from the organic group as a whole rather than from a single atom in the group. The entire topic has been exeellently reviewed by Cotton (31). Reinvestigations by Hein at this time lead him to agreement with this formulation of the structures for these compounds (32,33).

A series of theoretical papers in the nineteen fifties as exemplified by those of Coates and Glocking (34) and of Jaffe and Doak (35,36,37) advanced an explanation for the inability of chemists to prepare σ-bonded compounds and resulted in an entirely new direc-

tion in subsequent synthetic efforts. The arguments will be illustrated below for a hypothetical dialkyl compound of a transition metal.

In Figure 1, the molecular orbital diagrams for a σ-bonded dialkyl complex and for a dialkyltetracarbonyl complex are compared. The diagrams were constructed assuming a linear geometry for the dialkyl complex and an octahedral geometry for the dialkyltetracarbonyl complex. In each case, the alkyl groups are assumed to utilize sp^3 orbitals for bond formation to the metal. The carbonyl, CO, ligand is considered to donate electrons to the metal using an sp orbital on carbon; however, CO also has the ability to accept electrons from the metal atom into the empty antibonding (π*) orbitals of the CO π system. Electron occupation of the resulting molecular orbitals varies with the metal atom; however, for all the transition metals except Group IIIB elements, the non-bonding metal d orbitals will be occupied. Thus, in the carbonyl complex, the π molecular orbitals will also be occupied for these metals. The distance labeled E in each diagram therefore represents the energy of the lowest electronic transition of the compound. Calculations performed by Jaffe and Doak (35-37) using the simplifications implicit in Mulliken's "Magic Formula"

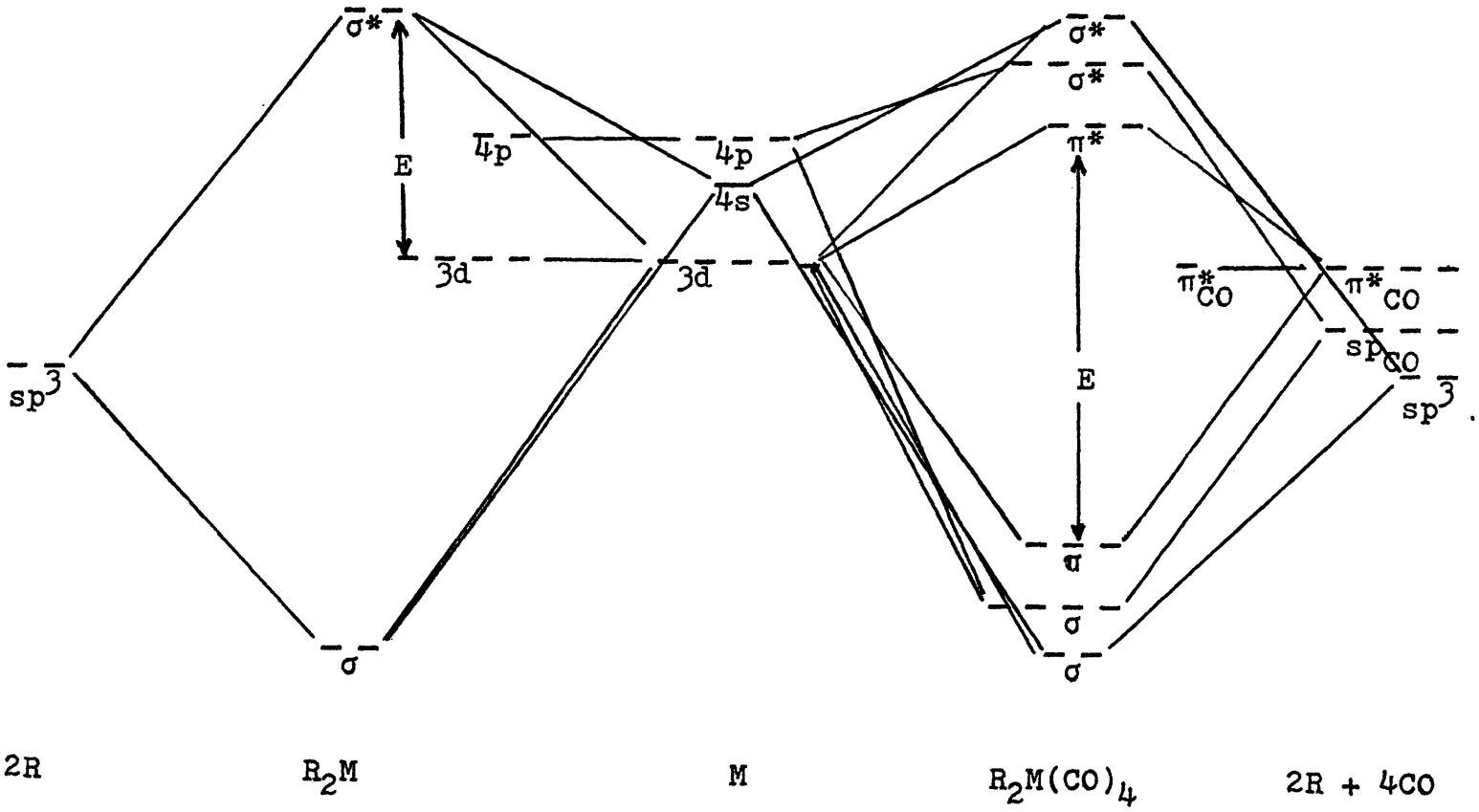


Figure 1. Molecular Orbital Diagrams for R_2M and $R_2M(CO)_4$

(38) estimated the value of E for σ-bonded transition metal alkyls to be of the order of magnitude of kT at normal temperatures. Thermal promotion of an electron to an antibonding orbital from one of these nonbonding levels thus weakens the bonding and ultimately leads to bond dissociation. The importance of this mode of decomposition is minimized in the carbonyl complex by the increase in E resulting from the involvement of the d orbitals in π bonding. Complexes of the carbonyl type are therefore expected to be more stable toward thermal decomposition than are simple alkyls.

The effect which such theoretical treatments had on the subsequent efforts in synthesis is indicated by the concluding statement of Richardson in his paper on the subject (39): "The present direction of synthesizing 'mixed' derivatives would seem most profitable. In choosing ligands to 'condition' the metal, π-bonding effects should be carefully considered. If the metal has nearly filled d-π orbitals, then ligands with predominately π-acceptor properties whould be considered; if the d-π orbitals are nearly vacant then π-donor ligands should be preferable." That such statements greatly affected experimental efforts is demonstrated by the enormous number of "mixed" complexes since reported.

General discussions of such complexes may be found in review articles and general references (31,34,39,40,41).

Despite the apparent validity of the above arguments, recently a number of "unstabilized" alkyls and aryls have been isolated including diphenylmanganese (42), dimethylmanganese (43), tri- and tetramethyltitanium (44), tetra- and diphenyltitanium (45), phenylcopper (46), methyl-, ethyl-, and propylcopper (47), triphenylchromium and triphenylchromium tristetrahydrofuranate (48-52), trimesityl- and trinaphthylchromium (53,54), and tribenzylchromium (55). Although these "unstabilized" species are generally less thermally stable than complexes containing π ligands, the limited stability that they do exhibit indicates that the mean bond energy calculations of Jaffe and Doak (35-37) presented an overly pessimistic view of the strength of the transition-metal-to-carbon σ bond.

The demonstration by Herwig and Zeiss (48,49) that σ-bonded phenylchromium compounds result from Hein's original method (1) if tetrahydrofuran rather than ethyl ether is used as the solvent stimulated new efforts by Hein and others in the synthesis of chromium alkyls and aryls. The result has been the preparation of an entire series of complex organochromium compounds (56-63) which appear to contain the anionic species $Cr(C_6H_5)_5^{=}$, $Cr(C_6H_5)_6^{3-}$,

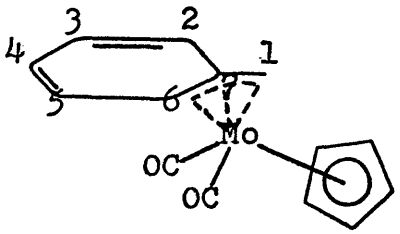
$Cr(CH_3)_6^{3-}$, $Cr(CH_3)_4^{=}$, $Cr(C_6H_5)_4^{-}$, $Cr(CH_3)_5^{=}$, $Cr(C_4H_8)_3^{3-}$, $Cr(C_5H_{10})_2^{=}$, $Cr(C_6H_5)_3^{-}$, and analogous species containing substituted aryl groups. Similar compounds of tungsten (64,65), niobium (66,67), and tantalum (68) have also been reported. Structural information on these compounds is still lacking; however, on the basis of meager spectrophotometric evidence, Hein has proposed (61) octahedral structures for the hexaphenyl- and pentaphenylchromate species. In the pentaphenylchromate anion, the sixth co-ordination site is occupied by a solvent molecule. If proven correct, this structure would necessitate considerable phenyl-to-chromium bond energy in view of the preferential bonding to phenyl in the presence of excess solvent molecules.

The above σ-bonded compounds are moderately stable to thermal decomposition; however, they are all exceedingly reactive compounds, often pyrophoric. By contrast, two remarkably stable and unreactive alkylchromium complexes have been reported by Anet (69,70). The ions, $Cr(H_2O)_5CHCl_2^{2+}$ and $Cr(H_2O)_5C_6H_5CH_2^{2+}$, are unreactive toward one molar perchloric acid solution and may be passed unchanged through ion exchange columns. This unreactivity has been attributed to the known substitution inertness of octahedral Cr (III) complexes rather than to strength

of the carbon-chromium bond.

Another recently reported compound of apparently abnormal properties is bis(triphenylmethyl)nickel (71). Thermal decomposition of this compound requires reasonably high temperatures and the solid is reported to be unreactive to air and water for days at room temperature. In the absence of air, this species is cleaved by aqueous hydrochloric acid only after twenty hours. These properties may be due to the large steric requirements of the triphenylmethyl group rendering substitution processes slow or electronic factors may be responsible as suggested by King (72).

King and Fronzaglia (73) studied the nuclear magnetic resonance spectrum of the compound, $C_6H_5CH_2Mo(CO)_2C_5H_5$, which results from photochemical decomposition of σ-$C_6H_5CH_2Mo(CO)_3C_5H_5$. They consider the spectrum to be consistent only with a pseudo-allylic benzyl ligand which donates π electrons to the σ orbitals of the metal atom.

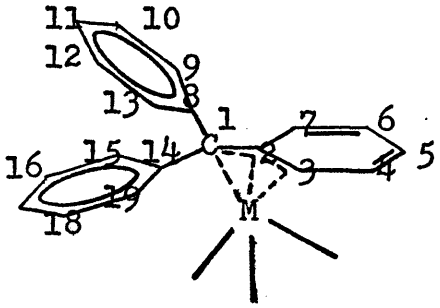


Four positions of attachment to carbons 1, 2, 6, or 7 are possible

Figure 2. The π-Allylic Benzyl Ligand

In this configuration, the resulting π* orbitals of the benzyl ligand may be used to accept d-π electrons from the metal. As previously discussed, this involvement of metal d electrons in the formation of π bonds to the ligands increases thermal stability of the complex.

King has proposed a similar π-allylic model for bis(triphenylmethyl)nickel (72). In the triphenylmethyl ligand, the allylic electrons could presumably be delocalized over a total of ten carbon atoms through fluxionality (74) analogous to that indicated above for the benzyl case. The nuclear magnetic resonance spectrum



Twelve positions of attachment are possible involving carbons 1, 2, 3, 7, 8, 9, 13, 14, 15, and 19.

Figure 3. The π-Allylic Triphenylmethyl Ligand

of bis(triphenylmethyl)nickel could prove the occurrence of this fluxional motion; unfortunately, this information has not yet been published.

The experiments described in the following section were designed to further investigate the nature of the

triphenylmethyl ligand in organo-transition-metal compounds. Bis(triphenylmethyl)nickel proved an unsatisfactory compound for the necessary physical measurements. Therefore, chromium systems were chosen because of the numerous recent successes in preparation of organochromium compounds.

EXPERIMENTAL WORK

The preparation and purification of reagents, the synthesis of organochromium compounds, the quantitative analysis of the organochromium compounds, and the measurement of physical properties of the organochromium compounds constitute the experimental work performed.

Preparation and Purification of Reagents

All materials not specifically discussed below were commercial "reagent grade" materials which were used without further purification.

Solvents. Tetrahydrofuran (THF) was distilled before use from lithium aluminum hydride ($LiAlH_4$). Benzene was allowed to stand for several days over Type 4A molecular sieves (Fischer Scientific Company) prior to use.

Triphenylmethylsodium. $NaC(C_6H_5)_3$ was prepared in ethyl ether solution by the method described by Hauser and Hudson (75). The required sodium amalgam was obtained from direct interaction of the elements at the melting point of sodium under a protective layer of min-

eral oil. The amalgam was washed with dry benzene immediately prior to use. Triphenylchloromethane was used as obtained from Arapahoe Chemicals Company of Boulder, Colorado.

Triphenylmethyllithium. $LiC(C_6H_5)_3$ was prepared in a manner analogous to that reported by Tomboulian (76). Lithium wire and a small amount of triphenylchloromethane in THF solution were stirred at reflux under a nitrogen atmosphere. When appearance of the red-orange color of the product signalled initiation of the reaction, then the remainder of the triphenylchloromethane was slowly added and the resulting mixture stirred at reflux for four hours to complete the reaction. The solution was stored in a tightly-stoppered flask.

Tris(2,4-pentandiono)chromium(III) and Tris(3-nitro-2,4-pentandiono)chromium(III). $Cr(C_5H_7O_2)_3$ was prepared by the method of Fernelius and Blanch (77) and was recrystallized from an ethanol-chloroform mixture before use. $Cr(C_5H_7O_2NO_2)_3$ was synthesized by the method of Collman, Marshall, Young, and Goldby (78) and was twice recrystallized from ethanol-chloroform.

Chromium(III) Chloride Tris(tetrahydrofuranate). A solution of $CrCl_3 \cdot 3THF$ in tetrahydrofuran was obtained as described by Angelici (79). The solution was used directly

without removal of the solvent.

Chromium(III) Iodide. CrI_3 was prepared by the reaction of aqueous HI with freshly precipitated $Cr(OH)_3$. The resulting hydrous product was recrystallized from methanol and then dehydrated by refluxing in 2,2-dimethoxypropane. The black crystals were stored in a desiccator over anhydrous calcium chloride.

Synthesis of Organochromium Compounds

All reactions were carried out in a 250 ml, three-necked flask equipped with addition funnel, stirrer, and two reflux condensers through which nitrogen gas was introduced and removed. A nitrogen atmosphere was maintained throughout all reactions.

Preparation of Sodium (Triphenylmethyl)pentacarbonylchromium. Two grams chromium hexacarbonyl ($Cr(CO)_6$) were placed in the reaction flask and the nitrogen atmosphere established. Through the addition funnel, 50 ml THF were added and the mixture stirred for several minutes to promote dissolution of some of the $Cr(CO)_6$. Then 100 ml of the ether solution of $NaC(C_6H_5)_3$ were added. The addition funnel was replaced with a stopper at this point. The resulting mixture was stirred at room temperature for 72 hours. During this time, most of the ether was lost to

evaporation through the reflux condensers.

After reaction, the flask was stoppered and removed to a dry bag filled with dry nitrogen. Unreacted $Cr(CO)_6$ was removed by filtration and the product precipitated with 100 ml hexane. The orange solid was collected on a sintered-glass filter and washed repeatedly with hexane, then with THF, and finally again with hexane. Washing with THF was possible as the solid exhibited little tendency to redissolve once precipitated. After drying in the nitrogen stream in the dry bag, the product was stored in nested, screw-top containers placed in a desiccator charged with anhydrous calcium chloride.

Preparation of Sodium (Triphenylmethyl)tricarbonylchromium. Upon mild warming of the solid, the $NaCr(CO)_5C(C_6H_5)_3$ described above loses two moles CO per mole being converted to $NaCr(CO)_3C(C_6H_5)_3$. This reaction also occurs slowly at room temperature. As will be discussed later, the ease of conversion to the tricarbonyl compound is due to the electronic changes accompanying the conversion.

Preparation of Bis(triphenylmethyl)chromium. The preparation of $NaCr(CO)_5C(C_6H_5)_3$ was repeated. When the reaction mixture had been filtered under nitrogen, the filtrate was returned to a reaction vessel and refluxed for several hours converting the product largely to the

tricarbonyl. Four grams triphenylchloromethane, $(C_6H_5)_3CCl$, were added and the solution stirred at reflux for 24 hours. The flask was then stoppered, removed to a dry bag, and the solution filtered to remove solids (NaCl). The product was precipitated with hexane, washed with hexane, and then dried. As this compound was shown to undergo no change upon exposure to air for prolonged periods, all subsequent operations were carried out in the atmosphere. The deep red solid was recrystallized from benzene and air dried. The product was stored in a desiccator over calcium chloride.

Repetition of this preparation under a variety of conditions demonstrated that addition of benzene to the reaction solution increases the reaction rate and improves yield of the product. Addition of catalytic amounts of tris(2,4-pentandiono)chromium to the reaction mixture also was found to speed the reaction. In all cases, the identity of the product (as indicated by the infrared spectrum) was the same.

Attempted Preparation of Bis(triphenylmethyl)-chromium by Other Reactions. Using analogous reaction conditions, preparation of $((C_6H_5)_3C)_2Cr$ was attempted through reaction of both $NaC(C_6H_5)_3$ and $LiC(C_6H_5)_3$ with tris(2,4-pentandiono)chromium(III), with tris(3-nitro-

2,4-pentandiono)chromium(III), with chromium(III) chloride tristetrahydrofuranate, and with chromium(III) iodide. Products were handled in a dry bag as described above.

Quantitative Analyses

Specific analytical data for the organochromium compounds are tabulated in the Appendix.

Chromium Analyses. Several methods were tried for chromium analysis. The method described below yielded the greatest reproducibility.

Weighed samples were gently boiled in 6N H_2SO_4 solution for about 30 minutes; two ml 30% H_2O_2 were then added and the solution allowed to cool for several minutes. The resulting triphenylmethyl peroxide was then removed by filtration and washed with dilute H_2SO_4 and then with water. The washings were combined with the filtrate.

The solution was made basic with KOH and an additional one ml 30% H_2O_2 added to oxidize the chromium to chromate. Excess H_2O_2 was destroyed by boiling the solution with precaution against losses from spattering. Reacidification of the solution with H_2SO_4 converted the chromate to dichromate. Excess KI was dissolved in the solution. The free iodine thus produced was titrated with standard

$$14\ H_3O^+ + Cr_2O_7^= + 6\ I^- = 3\ I_2 + 2\ Cr^{3+} + 21\ H_2O$$

$Na_2S_2O_3$ solution (standardized using potassium dichromate

$$2\ S_2O_3^{=} + I_2 = 2\ I^- + S_4O_6^{=}$$

as primary standard). Starch indicator was added to enhance the color change at the endpoint.

The chromium content of bis(triphenylmethyl)chromium was was determined by the above method and by direct ignition of the sample in a tared platinum crucible. Weighing the resulting Cr_2O_3 permitted direct calculation of the chromium content. This method proved unsatisfactory for the carbonyl compounds as mixtures of Cr_2O_3 and Na_2CrO_4 resulted from ignition.

Sodium and Lithium Analyses. Both sodium and lithium were determined by flame photometry. A Beckman Model B Spectrophotometer with flame attachment was used. The samples were boiled in dilute HCl solution for 30 minutes, and the insoluble organic material removed by filtration. The combined filtrate and washings were diluted to appropriate volume in a volumetric flask and the flame transmittance recorded. The %Na or %Li was then obtained from a standard curve recorded for standard solutions of the chlorides in dilute HCl solution. The standard curve was rerun for each analysis.

Triphenylmethyl Analyses. The total triphenylmethyl content of the samples was determined in two different ways.

Weighed samples were dissolved in concentrated H_2SO_4 and gently warmed for about 30 minutes (longer heating, 3 hours, was required for samples of bis(triphenylmethyl)-chromium). The solutions were then diluted to volume in a volumetric flask with H_2SO_4. The transmittance of the solutions at 430 mu due to the triphenylmethyl cation was then determined and compared to a standard curve for solutions of triphenylmethyl carbinol in H_2SO_4. Poor reproducibility of this method was presumably due to incomplete decomposition of the organochromium species or to possible spectrophotometric interference from some chromium species in solution.

Improved reproducibility was obtained in gravimetric determination of the triphenylmethyl content as triphenylmethyl peroxide. Samples were warmed gently for 30 minutes in a 6N H_2SO_4 solution containing H_2O_2. The resulting peroxide (confirmed by the infrared spectrum) was filtered, washed with water, dried at 110°C., and then weighed.

Carbon-hydrogen Analyses. Carbon and hydrogen were commercially determined by Schwartzkopf Microanalytical Laboratories, Woodside, New York.

Physical Measurements

The spectra and other data collected are included in the Appendix.

Infrared Spectra. All infrared spectra were recorded using a Perkin-Elmer Model 521 Spectrophotometer. Most spectra were obtained for the sample in KBr pellet form. Solution spectra were recorded using matched liquid cells with the solvent in the reference beam.

Visible and UV Spectra. These spectra were obtained using a Beckman Model DK-2 Spectrophotometer. Matched silica cells with solvent in the reference beam were used.

Nuclear Magnetic Resonance Spectra. A Varian Model A60-A NMR Spectrometer was used in attempting to obtain nuclear magnetic resonance spectra for the reported compounds. However, due to low solubilities of the compounds in appropriate solvents and to paramagnetic shifts in the proton resonances no resolvable NMR signals were observed for these compounds.

RESULTS AND DISCUSSION

The preparation of three new compounds, $NaCr(CO)_5C(C_6H_5)_3$, $NaCr(CO)_3C(C_6H_5)_3$, and $Cr(C(C_6H_5)_3)_2$, has been discussed in the preceeding section. The results of the measurement of the physical properties of these compounds provide the necessary data for the evaluation of the ligand characteristics of the triphenylmethyl group in chromium complexes.

As discussed in the "Introduction", thermal stability of organometallic complexes of the transition metals is strongly dependent upon the involvement of metal d orbitals in π bond formation. Of major importance, therefore, is the ability of the triphenylmethyl ligand to accept metal d electrons. This ability may be determined from the infrared spectra of the carbonyl compounds.

The CO ligand bonds to metal atoms through σ donation of carbon sp electrons and π acceptance of metal d electrons into the π^* antibonding orbitals of the C-O π system. Thus the increase in metal-carbon bond order due to π acceptance of metal d electrons is accompanied by a

decrease in carbon-oxygen bond order as the population of the antibonding orbitals increases. This weakening of the C-O bond is observed experimentally as a decrease in the CO stretching frequency for bonded CO as compared to free CO gas. The frequency in $Cr(CO)_6$ (1988 cm^{-1}) is, for example, much lower than that in free CO (2143 cm^{-1}).

In $Cr(CO)_6$, which has an octahedral structure, each CO ligand competes for d electrons primarily with the trans CO and to a lesser extent with the CO groups in cis positions. Therefore, if one of the CO ligands is replaced with a ligand of lower acceptor ability (which is the case for all known ligands with the apparent exception of PF_3) then the competition for d electrons among the remaining CO groups is lessened. The increase in population of π^* antibonding levels will be greatest for the trans CO group. The experimentally observed effect will be an increase in the number of CO stretching bands and a decrease in the band frequencies.

The expected number of bands may be readily deduced from group theory (80,81,82). The expected structure for the compound, $NaCr(CO)_5C(C_6H_5)_3$, would place the triphenylmethyl group and the five CO groups in octahedral sites of chromium. Therefore, the point group symmetry is C_{4v} if the inherent symmetry of the triphenylmethyl group is

disregarded. Using the five CO displacement vectors (corresponding to the stretching vibrational modes) as a basis set, the reducible representation of Group C_{4v} below is generated.

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
	5	1	1	3	1

By standard methods (80), this representation may be reduced to $2A_1 + B_1 + E$. In Group C_{4v}, the z vector transforms as A_1 and the x,y vectors as E. Therefore, the transition moment integrals for the A_1 vibrational modes with z polarization and for the E mode with x,y polarization of the excitation radiation do not vanish (82). These three modes are thus infrared active and three distinct stretching bands are expected in the infrared spectrum. The B_1 mode is not infrared active in Group C_{4v}; however, any inclusion of the inherent symmetry of the triphenylmethyl group would reduce the point group symmetry (to C_1) activating this mode.

The experimental infrared spectrum (see Appendix) of this compound in KBr pellet exhibits bands at 2065, 1942, and 1880 cm^{-1}. Band assignments are not straightforward in this case but do follow from the vibronic analysis below. The spectrum of this compound in THF solution also shows a weak band at 1980 cm^{-1}.

Cotton and Kraihanzel (83) have derived approximate secular equations for the vibrational energies of the CO stretching modes in substituted octahedral carbonyls of the Group VIB elements. Only non-mechanical coupling of the CO groups is considered and no anharmonicity corrections are made. The potential energy matrices are written in terms of the necessary number of stretching constants and a single interaction constant. This single interaction constant is introduced by assuming that all cis interactions are equivalent and the constants for all trans interactions are twice the cis interaction constants. This relationship follows from the consideration that cis pairs share one d-π orbital while trans pairs share two. These approximations appear to present no limitation to the vibronic analysis of $NaCr(CO)_5C(C_6H_5)_3$ if the triphenylmethyl group is assumed to be symmetrically situated with respect to cis CO groups as would be expected on steric grounds. The approximate secular equations are:

$$A_1: \quad \begin{vmatrix} uk_1-\lambda & 2uk_i \\ 2uk_i & u(k_2+4k_i)-\lambda \end{vmatrix} = 0$$

$$E: \quad \lambda = u(k_2-2k_i)$$

$$B_1: \quad \lambda = uk_2$$

where u is the reduced mass of CO (.14583), k_i is the interaction constant, k_1 and k_2 are the stretching constants,

and $\lambda = .05889\nu^2$ where ν is the band frequency in cm^{-1}. Solution of these equations using $\nu(A_1) = 2065\ cm^{-1}$, $\nu(A_1') = 1880\ cm^{-1}$, and $\nu(E) = 1942\ cm^{-1}$ yields the following values for the constants:

$k_1=14.41$ $k_2=15.85$ and $k_i=0.32$ (mdyne/Å)

Inserting the above values into the secular equation for the B_1 mode yields $\nu(B_1) = 1981\ cm^{-1}$. All other possible band assignments yield k_1 greater than k_2 which is not permisible as k_1 is the trans stretching constant which, as discussed above, must be lowered more than the cis constant, k_2.

The π-acceptor ability of the triphenylmethyl group in this compound may be deduced by comparing the above stretching constants to those for similar monosubstituted octahedral carbonyls. As the trans constants, k_1, are more greatly affected than are the cis, k_2, or the interaction, k_i, constants, comparison of the k_1 values is most informative. For the purpose of this comparison, the calculated constants for several compounds using data from the literature (84,85) are tabulated below. The values for the trichlorophosphine, triphenoxyphosphine, and dimethylformamide ligands are for the molybdenum compounds. The others are for the chromium compounds. For a given ligand, the force constants for the molybdenum and for the

chromium compounds are essentially the same (84).

Ligand	k_1	k_2	k_i
PCl_3	16.38	16.46	0.26
$P(OC_6H_5)_3$	15.62	16.02	0.30
$P(C_6H_5)_3$	15.50	15.88	0.33
$C_6H_{11}NH_2$	14.59	15.77	0.32
Cl	14.06	15.58	0.34
DMF	13.93	15.67	0.36

Table 1. Stretching constants (mdyne/Å) for some monosubstituted octahedral carbonyl complexes

The π-acceptor ability of the triphenylmethyl ligand in $NaCr(CO)_5C(C_6H_5)_3$ is therefore similar to that of cyclohexylamine and less than that of the phosphine ligands.

For the compound, $NaCr(CO)_3C(C_6H_5)_3$, the three CO ligands may occupy either cis or trans positions. For the cis case, the point group symmetry is C_{3v} and the reducible representation generated from the CO displacement vector set is:

C_{3v}	E	$2C_3$	$3\sigma_v$
	3	0	1

This representation reduces to $A_1 + E$. In Group C_{3v}, the z vector transforms as A_1 and the x,y vectors as E. Thus two CO stretching bands are expected in the infrared spectrum.

For the trans case, the point group symmetry is C_{2v} and the generated reducible representation is:

C_{2v}	E	C_2	σ_v	σ_v'
	3	1	3	1

This representation reduces to $2A_1 + B_1$. The z vector transforms as A_1 and the x vector as B_1 in Group C_{2v}. Thus three CO stretching bands are expected in the infrared spectrum.

The experimental infrared spectrum of $NaCr(CO)_3C(C_6H_5)_3$ (see Appendix) shows two distinct bands and thus corresponds to the cis case. The approximate secular equations for the cis case are:

$$A_1: \quad \lambda = u(k+2k_i)$$

$$E: \quad \lambda = u(k-k_i)$$

Since k_i must be positive (83), only one assignment of the observed bands, $\nu(A_1)=1962$ cm^{-1} and $\nu(E)=1886$ cm^{-1}, is possible. The calculated stretching constants with this assignment are:

$$k = 14.75 \text{ and } k_i = 0.39 \text{ (mdyne/Å)}$$

These values may be compared with those for various trisubstituted carbonyls of this geometry from the literature (84). Again, the literature values were calculated from data for either the chromium or molybdenum compounds. In these carbonyls, Cotton has demonstrated (84) that a definite

decrease in k_i as well as an increase in k is observed as the π-acceptor ability of the substituted ligand increases.

Ligand	k	k_i
PF_3	16.98	0.33
PCl_3	16.27	0.27
$P(OC_6H_5)_3$	15.26	0.50
$P(C_6H_5)_3$	14.35	0.47
CH_3CN	13.45	0.64

Table 2. Stretching constants (mdyne/Å) for some trisubstituted cis octahedral carbonyl complexes

The π-acceptor ability of triphenylmethyl in $NaCr(CO)_3C(C_6H_5)_3$ is then comparable to that of triphenylphosphine and triphenoxyphosphine and considerably greater than that of acetonitrile.

This difference in π-acceptor ability of the triphenylmethyl ligand in the tri- and pentacarbonyl compounds implies a difference in the bonding mode in the two compounds. The low acceptor strength in the pentacarbonyl would be expected for a purely σ-bonded triphenylmethyl group where the ring antibonding levels are unavailable for π participation. The increase in acceptor strength in the tricarbonyl must then be the result of phenyl ring participation in bonding to the chromium.

Several possible models for involvement of the rings

must be considered. Hexahapto (86) π bonding analogous to that shown (25-30) to occur in the polyphenyl compounds reported by Hein (1-22) seems unlikely. For the triphenylmethyl ligand, such bonding would require the localization of an electron pair in an sp^3 orbital on the methyl carbon. A localized electron pair on carbon, even allowing for a

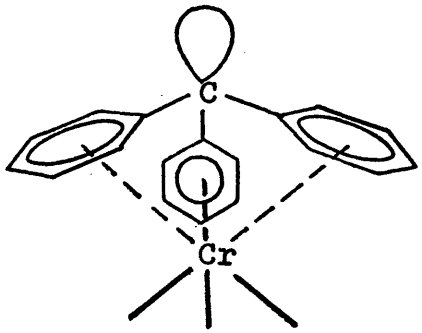


Figure 4. Hexahapto, π-bonded triphenylmethyl ligand

large inductive effect due to the electropositive metal atom, should be highly basic. The low reactivity of $NaCr(CO)_3$-$C(C_6H_5)_3$ with protic reagents (water, dilute acids, and concentrated sulfuric acid) is therefore not consistent with this model. Combination of hexahapto π bonding with σ donation of the sp^3 pair to an additional co-ordination site may be discarded in view of the required tetrahedral geometry of an sp^3 carbon.

A second possibility is the attachment of the triphenylmethyl group to the metal atom with two sigma bonds through loss of one ortho hydrogen. Pi interaction with

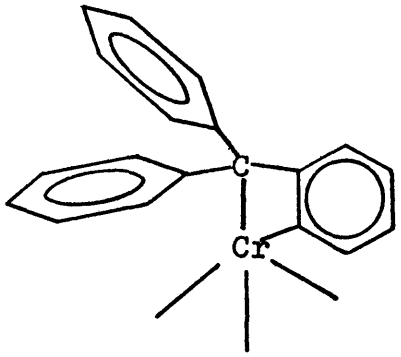


Figure 5. Doubly σ-bonded triphenylmethyl ligand

the σ-bonded ring could also contribute in this orientation. However, utilization of the π orbitals of the other two rings would require classical tautomerism, the actual movement of a hydrogen atom to a different site in the molecule. Such processes are expected to be slow and greater π-acceptor ability should result for the π-allyl model proposed by King for bis(triphenylmethyl)nickel (73).

Fluxionality of the π-allylic triphenylmethyl group could, as discussed in the "Introduction", provide involvement of all three phenyl rings in the bonding to chromium. This fluxional behavior delocalizes the sp^3 electron pair of the hexahapto model over ten carbon atoms decreasing the basicity of the electron pair greatly. The soundness of this model is further established by recent studies on the dimerization of the triphenylmethyl free radical (87). The radicals dimerize through attack at the

para position of a phenyl group requiring an electronic rearrangement similar to that required for the π-allyl model.

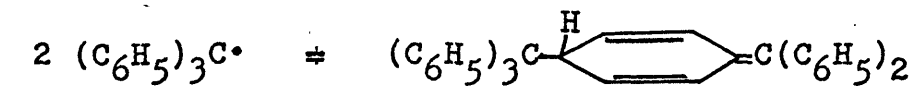


Figure 6. Dimerization of triphenylmethyl radical

The possibility of π-allylic bonding of one ring combined with any dπ-pπ interaction of the metal atom with another ring may be ruled out on steric grounds. Examination of a scaled molecular model of the compound indicates the impossibility of the required geometric arrangements.

The π-allyl model is also proposed to apply in $Cr(C(C_6H_5)_3)_2$. The properties of this compound suggest very low polarity of the metal-carbon linkages as expected for the π-allyl model. $Cr(C(C_6H_5)_3)_2$ reacts only slowly with water and dilute mineral acids in the presence of air and is apparently inert to these reagents in the absence of air. Cleavage of the compound produces triphenylmethyl peroxide rather than triphenylmethane as expected for a σ compound. The compound dissolves in cold concentrated H_2SO_4 with only partial conversion to the triphenylmethyl carbonium ion. Mild heating for several hours is required to complete the conversion. Similar unreactivity was reported

by Wilke for $Ni(C(C_6H_5)_3)_2$ (71); however, samples of this latter compound prepared in this study exhibited greater reactivity than reported. Reaction with air was found to be sufficiently rapid that isolation of the product free of triphenylmethyl peroxide and other decomposition products was not achieved even when this material was handled in a dry box. This air-sensitivity hampered efforts to obtain useful infrared and nuclear magnetic resonance spectra.

The selection of the π-allyl model for the bonding in bis(triphenylmethyl)chromium again requires consideration of several other possibilities. The π-hexahapto and other alternative models discussed for the tricarbonyl compound may be discarded on the same grounds. Simple σ bonding of the triphenylmethyl groups to chromium is rejected for several reasons. The arguments presented in the "Introduction" demonstrate that complexes in which the d orbitals of the metal atom remain nonbonding are inherently unstable to thermal decomposition. No evidence for thermal decomposition of $Cr(C(C_6H_5)_3)_2$ to 250°C. was found. Secondly, the presence of nonbonding d orbitals on chromium would provide sites for rapid attack of the complex by co-ordinating reagents such as water. Finallly, since the bis-(triphenylmethyl)chromium was prepared from the carbonyl compound, replacement of the strongly π-accepting CO ligands

with a ligand of low acceptor ability is very unlikely.

Finally, a model unique to the bis(triphenylmethyl)-chromium stoichiometry must be considered. The dimerization of two triphenylmethyl groups in the fashion discussed above provides a molecule with interesting possibilities as a ligand. Hexahapto π-bonding to two of the phenyl rings producing a "sandwich" compound is an attractive model. However, study of a scaled molecular model reveals considerable steric hindrance to the required geometric arrangement.

Thus, in the absence of direct structural data, the π-allyl model is proposed as most consistent with the observed properties. Collection of X-ray or low-temperature nuclear magnetic resonance data is prevented by the physical properties of the compounds. Unfortunately, a vibronic analysis of the infrared activity of the triphenylmethyl unit in these compounds is impossible due to the very large number of variables involved. However, comparison of the band frequencies of these compounds with those of other triphenylmethyl compounds is interesting. In Table 3, the observed bands in the ring-deformation region of the spectrum are tabulated for several compounds. All frequencies were determined for the sample in KBr pellet using the Perkin Elmer Model 521 Spectrophotometer.

Compound	Band Frequencies (cm^{-1})
$(C_6H_5)_3CCl$	750,740,730,693,660,633,620,612
$(C_6H_5)_3CH$	751,728,693,651,613,600
$((C_6H_5)_3CO)_2$	767,750,694,642,629
$((C_6H_5)_3CO)_2CrO_2$	755,694,634
$NaCr(CO)_5C(C_6H_5)_3$	756,742,728,695,652,638,631,605
$NaCr(CO)_3C(C_6H_5)_3$	753,738,699,656,634,613,602
$((C_6H_5)_3C)_2Cr$	770,757,752,702,648,633,608

Table 3. Ring-deformation frequencies in some triphenylmethyl compounds

The band near 700 cm^{-1} is clearly at a higher frequency in the two compounds proposed to contain the π-allylic triphenylmethyl group. These data were all for the KBr pellet form; therefore, the shifts cannot be due to solvent effects. Unfortunately, no report of the infrared spectrum of bis(triphenylmethyl)nickel has yet been published which might indicate whether this higher frequency is characteristic of the π-allyl case. Infrared spectra for samples of the nickel compound prepared in this study all contained two bands near 700 cm^{-1} undoubtedly due to decomposition. One band was higher (701 cm^{-1}) than expected for any decomposition product.

This higher frequency band near 700 cm^{-1} was also found for products of the reaction of either $NaC(C_6H_5)_3$ or

$LiC(C_6H_5)_3$ with $Cr(C_5H_7O_2)_3$. The products were also similar in appearance to bis(triphenylmethyl)chromium but all efforts to separate the products from high concentrations of alkali metal ion failed. These materials may be adducts although no characteristic stoichiometry was determined.

No definite organochromium species were isolated from reactions using the chromium halides although the triphenylmethyl reagent was apparently destroyed. In all cases green solids with high alkali metal ion content were obtained. The insolubility of the solids prevented purification.

The success of the carbonyl method of preparation for bis(triphenylmethyl)chromium is rather remarkable. The conversion apparently requires electrophillic attack by triphenylchloromethane on a carbonylate anion as triphenylchloromethane was found not to react with chromium hexacarbonyl. Presumably, the reaction also requires considerable interaction of the ring π orbitals with the metal atom labilizing the CO ligands. Thus the applicability of the method as a general preparative route may be limited.

In conclusion, the stabilities and low reactivities of $Cr(C(C_6H_5)_3)_2$ and $NaCr(CO)_3C(C_6H_5)_3$ are attributed to low polarity of the chromium-carbon bond resulting from π-allylic

bonding of the triphenylmethyl ligand. The low solubility of these compounds in polar solvents suggest that substitution inertness may also contribute to the low reactivity (but not, of course, to the thermal stability). The triphenylmethyl ligand is apparently an excellent system for the investigation of fluxional behavior having twelve possible positions of attachment. Synthesis of diamagnetic, π-allylic triphenylmethyl compounds of reasonable solubility would allow low-temperature nuclear magnetic resonance studies of the fluxional motion. The method of preparation reported here may provide the needed route to such compounds.

APPENDIX

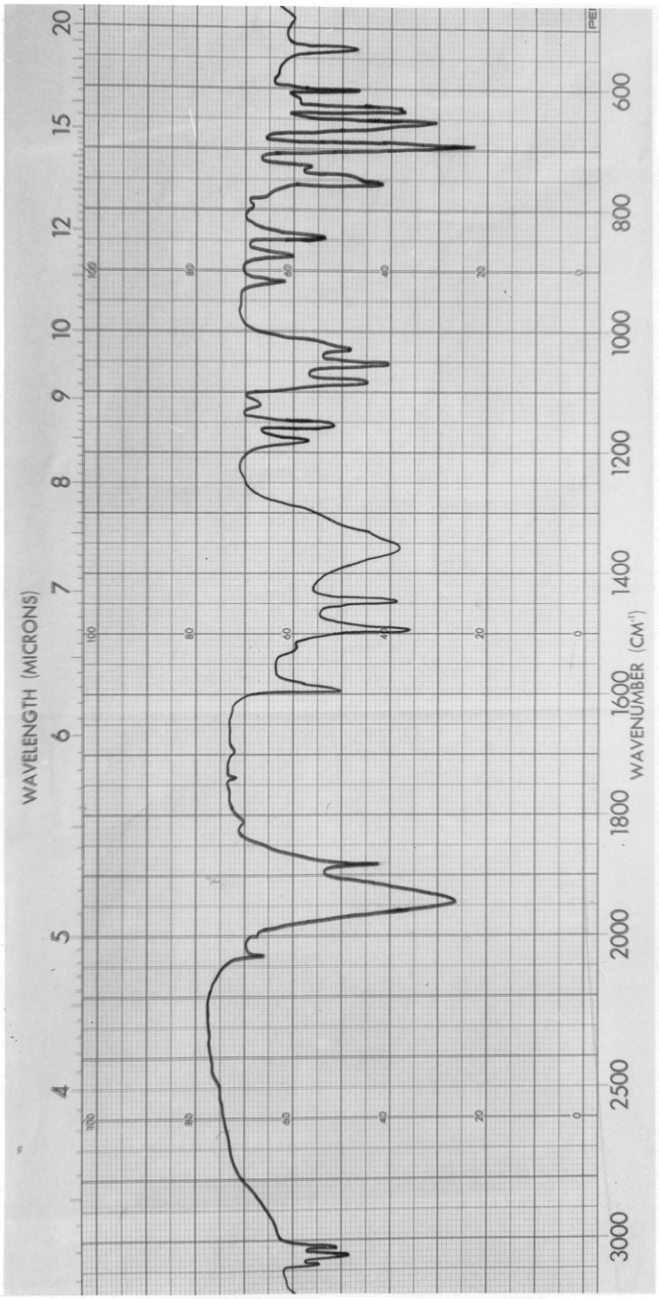


Figure 7. Infrared Spectrum (KBr) of $NaCr(CO)_5C(C_6H_5)_3$

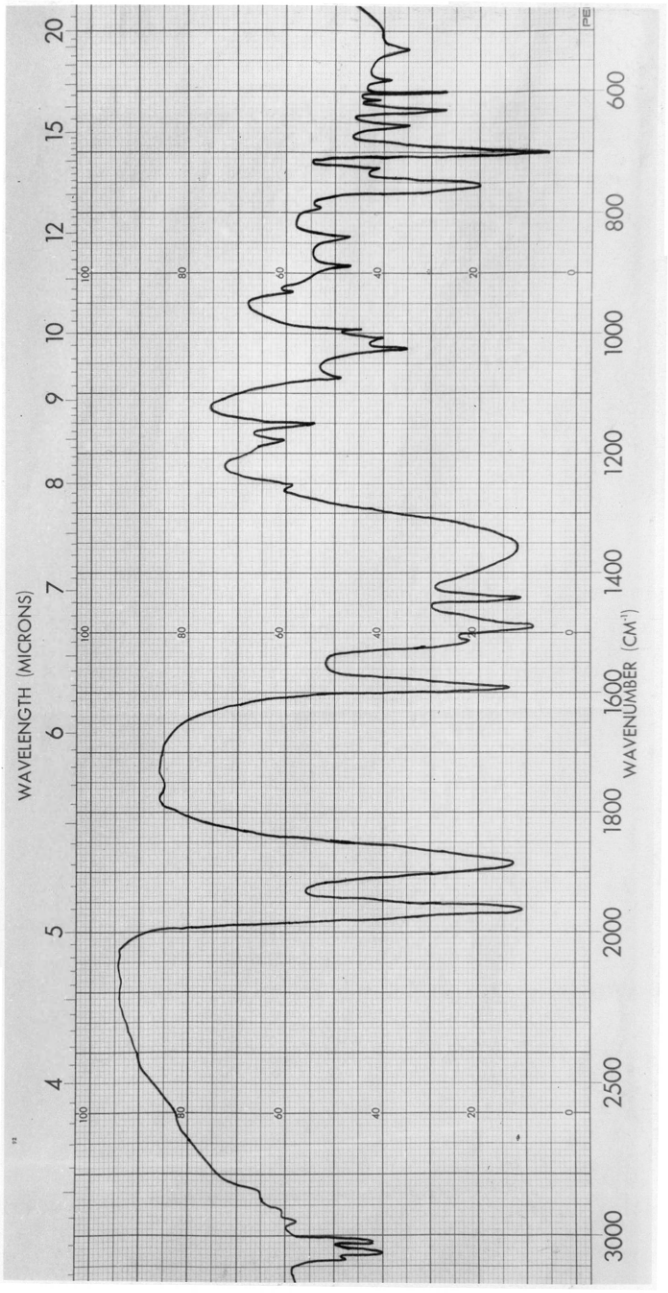


Figure 8. Infrared Spectrum (KBr) of $NaCr(CO)_3C(C_6H_5)_3$

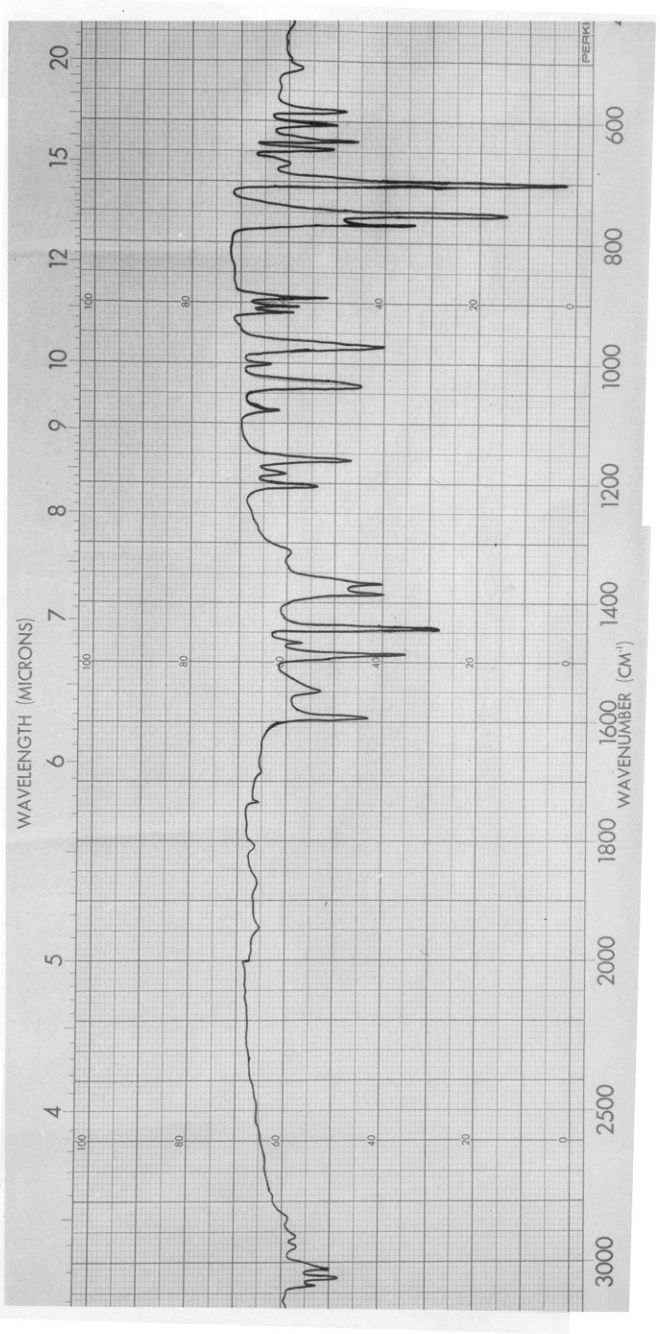


Figure 9. Infrared Spectrum (KBr) of $Cr(C(C_6H_5)_3)_2$

Table 4. Summary of the properties of $NaCr(CO)_5C(C_6H_5)_3$

State: Light orange solid

Composition: 5.10 %Na (5.02), 11.31 %Cr (11.35), 52.99 $\%C_{19}H_{15}$ (53.08). Theoretical values are in parentheses.

Thermal stability: Readily decomposed to $NaCr(CO)_3C(C_6H_5)_3$ with mild heating.

Chemical reactivity:

Reagent	Result
air	Spontaneously inflames
H_2O	Dissolves with partial con version to triphenylmethane
CH_2Cl_2	Reacts producing unidentified green solids
H_2SO_4	Violent reaction producing tri-phenylmethyl carbonium ion

Table 5. Summary of the properties of $NaCr(CO)_3C(C_6H_5)_3$

State: Light green solid

Composition: 5.67 %Na (5.72), 12.95 %Cr (12.93), 60.52 $\%C_{19}H_{15}$ (60.47), 65.62 %C (65.68), 4.03 %H (3.76). Theoretical values are in parentheses.

Thermal stability: Stable to 250°C.

Chemical reactivity:

Reagent	Result
H_2O	No apparent reaction
H_2O+air	Slow formation of $((C_6H_5)_3CO)_2$
Dilute HCl	No apparent reaction
Concentrated H_2SO_4	Dissolution with slow conversion to triphenylmethyl carbonium ion
C_6H_6	Insoluble, slow reaction with complete loss of CO -- other products not identified
CH_2Cl_2	Insoluble, slow reaction with complete loss of CO -- other products not identified
$(C_6H_5)_3CCl$	Reacts in THF/C_6H_6 solution producing bis(triphenylmethyl)chromium

Table 6. Summary of the properties of $Cr(C(C_6H_5)_3)_2$

State: Deep red solid

Composition: 9.68 %Cr (9.65), 90.28 $\%C_{19}H_{15}$ (90.34), 84.61 %C (84.74), 6.34 %H (5.61). Theoretical values are in parentheses.

Thermal stability: Stable to 250°C.

Visible spectrum: Absorbance at 570 mu and strong charge transfer absorbance below 500 mu

Chemical reactivity:

Reagent	Result
H_2O	No apparent reaction
Dilute HCl	No apparent reaction
H_2O+air	Slow formation of $((C_6H_5)_3CO)_2$
Concentrated H_2SO_4	Dissolution with slow conversion to triphenylmethyl carbonium ion
O_2	No apparent reaction in benzene solution
C_6H_6	Slightly soluble, no apparent reaction
CH_2Cl_2	Insoluble, no apparent reaction

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