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Richard Alan Hall
Iowa State University

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Synthesis and reactivity of some chromium complexes containing chelating-arene ligands

by

Richard Alan Hall

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Graduate Faculty in Partial Fulfillment of
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HISTORICAL

The century and a half of transition metal organometallic chemistry following the synthesis of $K(PtCl_3C_2H_4)$ by Zeiss (1) has provided many thousands of stable metal complexes. These compounds are important to the organic chemist since many have displayed catalytic activity, providing new ways to prepare organic molecules. Both stable and unstable (highly reactive) organic ligands have seen complexed, luring the chemist to investigate these areas further.

One investigation has led to the discovery of the first arene metal complex, (benzene)tricarbonylchromium, by Fischer (2) from reaction of benzene with hexacarbonylchromium. The number of derivatives of this yellow crystalline compound which have subsequently been prepared is large and analogous compounds with other metals in place of chromium such as molybdenum and tungsten have also been characterized (3). Most arene tricarbonylchromium complexes have been synthesized in one of two ways; reaction of the free arene ligand with hexacarbonylchromium in refluxing solvents (4), or reaction of the free arene ligands with (triacetonitrile)-tricarbonylchromium (5).

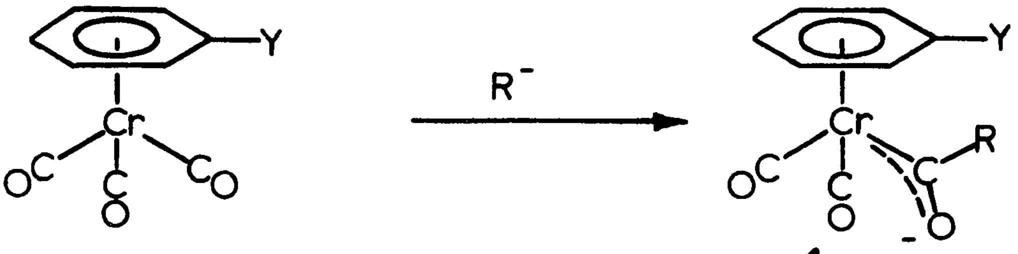
Other neutral complexes with cyclic π-systems other than benzene π-bonded to metal atoms have been prepared. These include (cyclobutadiene)tricarbonyliron (6), (cyclopentadienyl)tricarbonylmanganese (7), and (cycloheptatrienyl)tricarbonylvanadium (8).

Physical and Chemical Properties of Arene-tricarbonylchromium Complexes

With relatively low melting points and high solubility in organic solvents the arene-tricarbonylchromium complexes which have been investigated more closely resemble organic compounds than inorganic compounds. Many have displayed moderately high vapor pressure so that mass spectral data have been obtained and the spectra usually show a parent ion with peaks corresponding to successive loss of the three carbonyls (9). The solubility of the complexes has allowed investigation of the proton nuclear magnetic resonance (nmr) spectra of the compounds with the most striking feature being the two to three parts per million (ppm) shift to high field of the signals due to the metal-bound aromatic ring hydrogens compared to the chemical shift of the hydrogens of the uncomplexed ring in the same solvent (10). Infrared (ir) spectra have shown two very strong carbonyl bands in the range of 2100 to 1800 cm^{-1} (11).

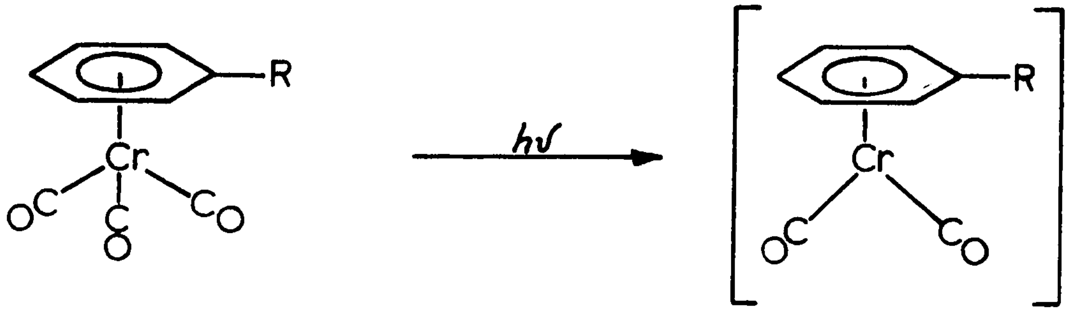
Chemical properties of the arene-tricarbonylchromium complexes resemble those of the free organic ligands. Indeed many of the same reactions of the free aromatic compounds have been successfully carried out on the analogous complexes. Noticeable differences, owing to the electron withdrawing nature of the tricarbonylchromium moiety, have included increased acidity of the complexed ring hydrogens and the hydrogens alpha to the complexed ring compared to the free arene ligands (12). The free arene ligands have been removed intact from the arene complexes using a variety of conditions: namely; ultraviolet light (13), cerium(IV) (14), or iodine (15).

A variety of chemical reactivity of the arene complexes is associated with the tricarbonylchromium moiety. It has been found that the carbonyl ligands of some complexes are subject to nucleophilic attack forming "carbene" complexes. The reaction works best when a good electron donating group, Y, is substituted on the ring. The anion (1) can be captured by the addition of a good alkylating agent. Carbene metal complexes have received considerable attention in recent years (16).



1

The arene-tricarbonylchromium compounds have been found to undergo facile photodecarbonylation reactions (17) forming the co-ordinatively unsaturated chromium species, 2. Strohmeier (10, 18, 19, 20) has utilized this property to prepare



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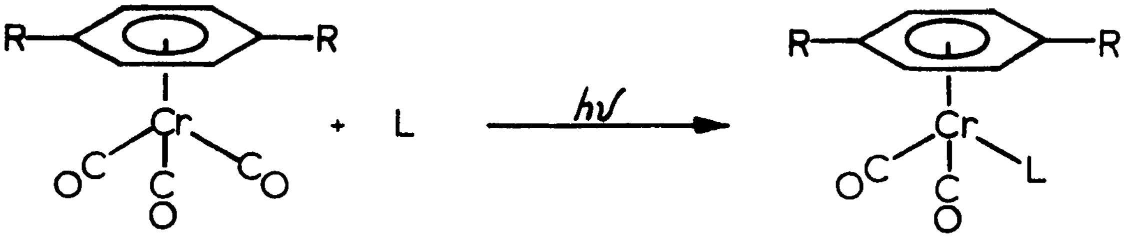
complexes with the general formula of 3 by photolysis of the corresponding tricarbonylchromium complexes in the presence of the ligand, L. Table I summarizes the representative examples of 3 prepared by this method.



3

When the ligand is an amine the complexes possessing structure 3 are formed when R is a strongly electron withdrawing group such as carbomethoxy, but have not been isolated when R is hydrogen (18). When the ligand is an alkene the complexes (3) are unstable when R is carbomethoxy; but are isolable when R is hydrogen. For example, (p-dicarbomethoxybenzene)-(ethylene)dicarbonylchromium has only been detected by ir spectroscopy, whereas (benzene)(ethylene)dicarbonylchromium has been isolated and characterized by elemental analysis as

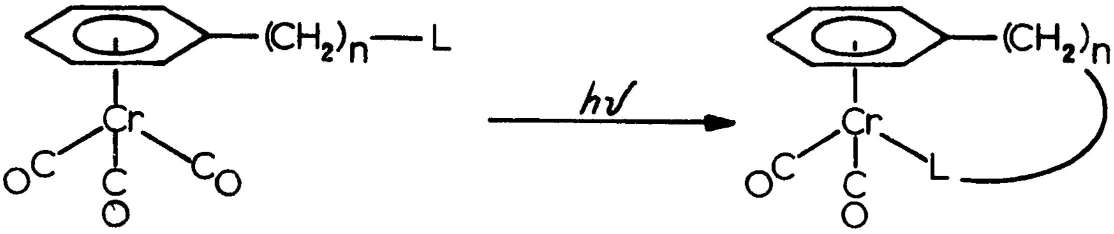
Table I. Representative examples of (benzene)(ligand)dicarbonylchromium complexes and (*p*-dicarbomethoxybenzene)(ligand)dicarbonylchromium complexes.

Arene	Ligand	Reference
benzene	ethylene	20
benzene	cyclopentene	20
benzene	pyridine	19
benzene	quinoline	10
benzene	triphenylphosphine	19
p-dicarbomethoxybenzene	acetonitrile	18
p-dicarbomethoxybenzene	aniline	18
p-dicarbomethoxybenzene	cyclohexylamine	19
p-dicarbomethoxybenzene	diphenylacetylene	20
p-dicarbomethoxybenzene	phenyl isonitrile	10

well as ir spectroscopy (20). (Hexamethylbenzene)(ethylene)-dicarbonylchromium (21) has also been isolated and has been found to be only slightly air sensitive. The alkene ligand is in general labile in the (arene)(alkene)dicarbonylchromium complexes as indicated by the rapid and quantitative displacement of ethylene from (hexamethylbenzene)(ethylene)dicarbonylchromium by triphenylphosphine (20).

Arene-chelate Complexes

The photolysis method used in the preparation of 3 seems to be fairly general. However, no examples have appeared in the literature where this method has been used to prepare arene-chelate complexes, those where a functional group, L, is bonded to a metal atom and connected to a metal-bound aromatic ring by a chain of atoms not including the metal atom (4).



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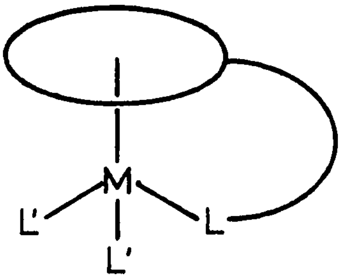
In general terms 4 can be represented as structure 5.



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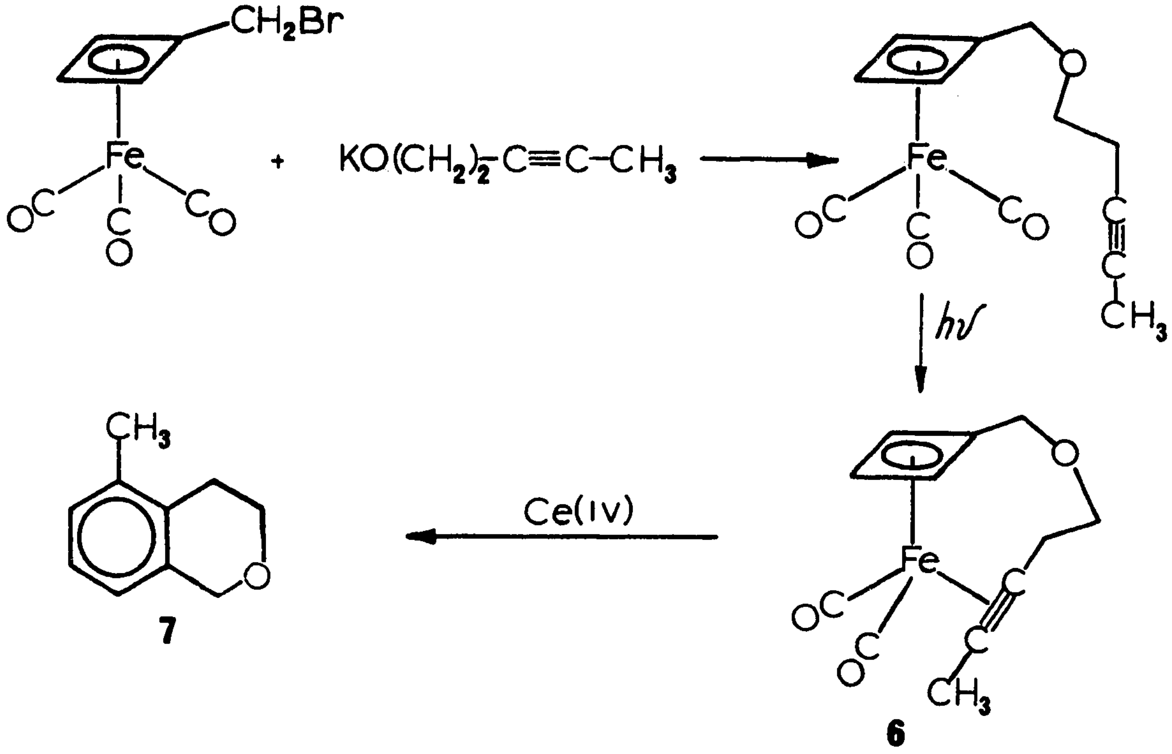
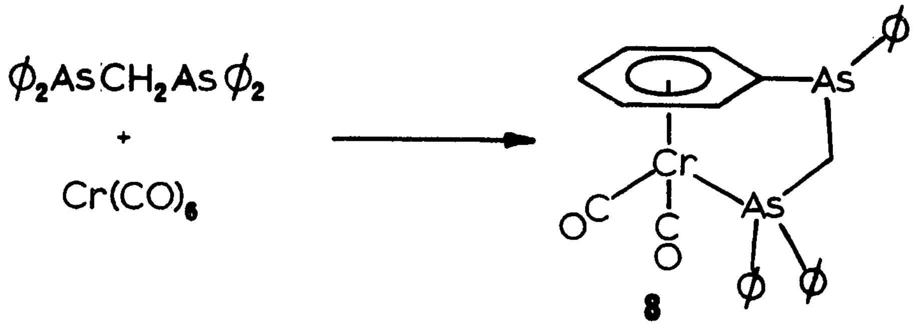
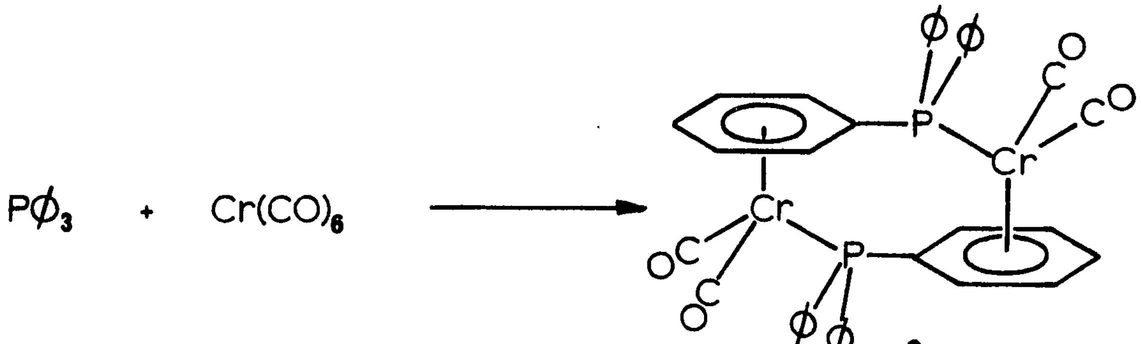
Grubbs (22) has postulated such a structure (6) as an intermediate in the reaction sequence converting (α-bromomethylcyclobutadienyl)tricarbonyliron to the benzopyran derivative, 7.



In the chromium series (Cr, Mo and W) only one arene-chelate complex has appeared in the literature (23, 24).

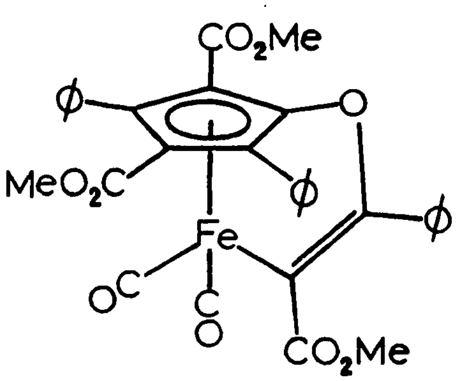


The reaction leading to 8 does not appear to represent a general route to arene-chelate complexes. However, a study has not been reported concerning the reactivity of a wide variety of other ligands capable of forming arene-chelate complexes when heated with hexacarbonylchromium. One problem with such an approach is dimer formation, as treatment of triphenylphosphine with hexacarbonylchromium has provided 9, a dimeric material (25).



9

Dahl (26) through reaction of methyl phenylpropiolate and diiron nonacarbonyl has produced the arene-chelate complex possessing structure 10. The complex has been characterized by ir, proton nmr, elemental analysis, and X-ray analysis, but occurred as only a minor component of the reaction product mixture.



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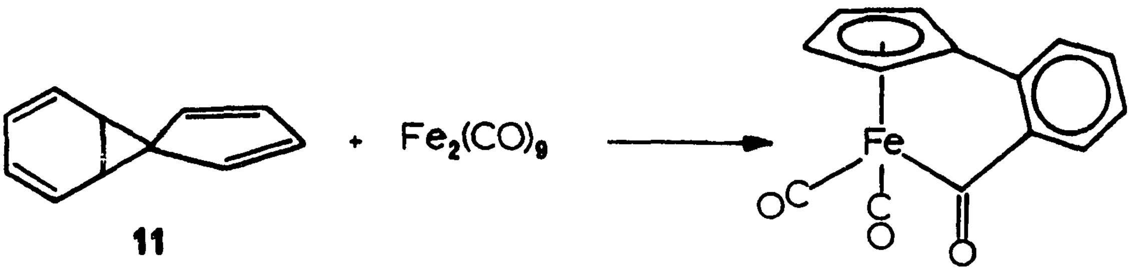
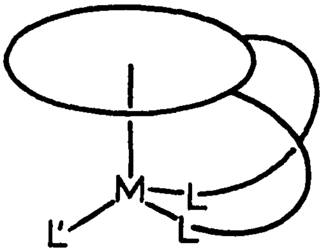
Moriarty (27) has investigated the reaction of the tricyclic compound 11 with diiron nonacarbonyl in ether at reflux for

30 hr, which produced still another arene-chelate complex (**12**) in low yield.



11 **12**

The reported reactions which have led to arene-chelate complexes reveal that no general method for preparing such compounds has appeared in the literature and no studies of the chemical reactivity of arene-chelate complexes have been made. Furthermore, no chelate complexes possessing the general structures **13** or **14** have appeared (28).



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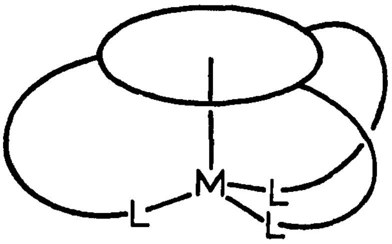
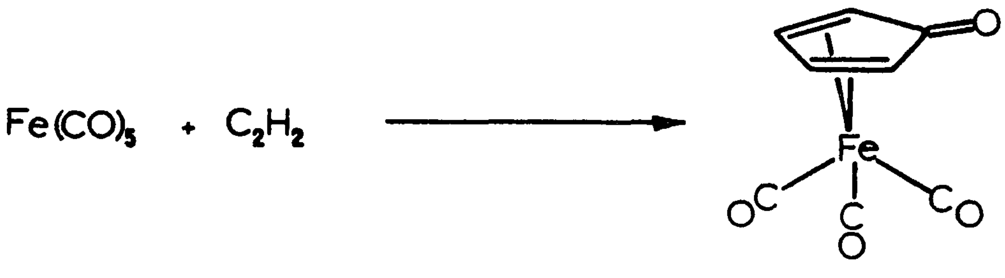


14

(Cyclopentadienone)tricarbonyliron, (Cycloheptatrienone)tricarbonylchromium and Derivatives

Metal complexes of cyclopentadienone and cycloheptatrienone have been prepared and their chemistry investigated.

Reppe (29) has found that parent (cyclopentadienone)tricarbonyliron (15) is one of the products from the thermal reaction of pentacarbonyliron and acetylene in alcohol solvent at high pressure. More recently, 15 has been prepared by reaction of cyclopentadienone diethyl ketal with diiron nonacarbonyl (30).



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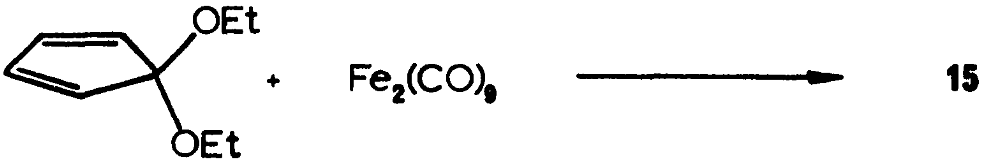
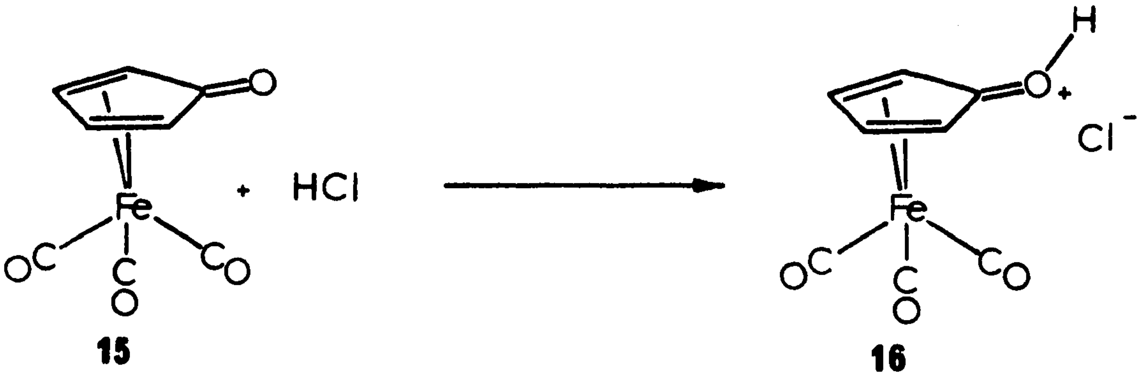
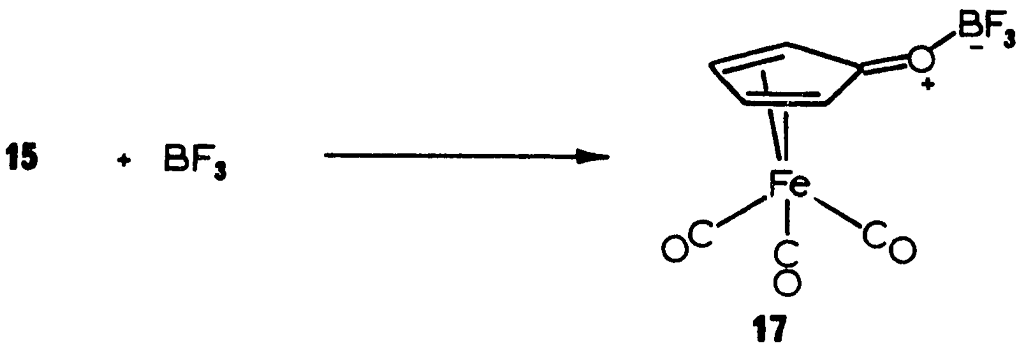


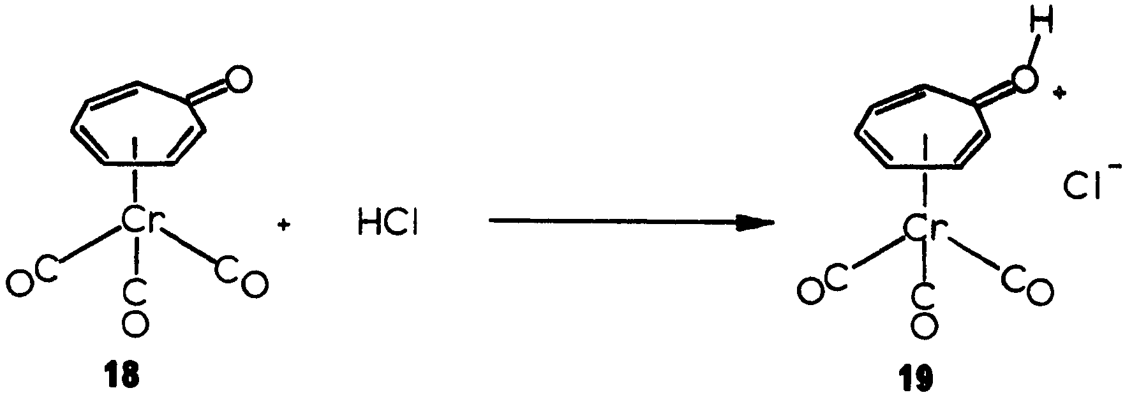
It has been suggested that complexing the cyclopentadienone ligand increases the polarity of the ketone group (31, 32) which explains much of the chemistry of 15 as studied mostly by Weiss (33). Complex 15 has been protonated using mineral acids producing stable salts such as 16. The complex (15) has also been shown to undergo reaction with



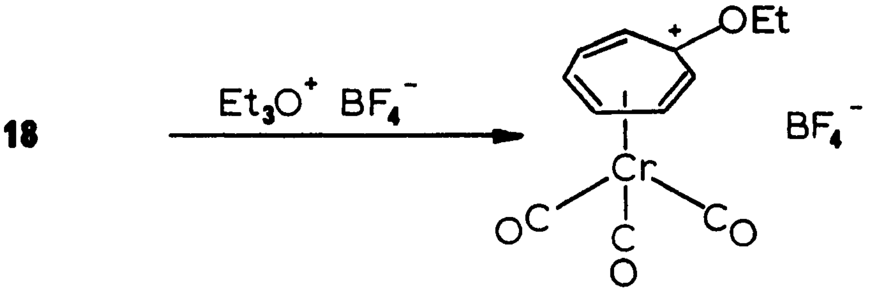
Lewis acids to give stable adducts such as 17. Other derivatives of 15 have been prepared where phenols supply a proton and a salt is formed.



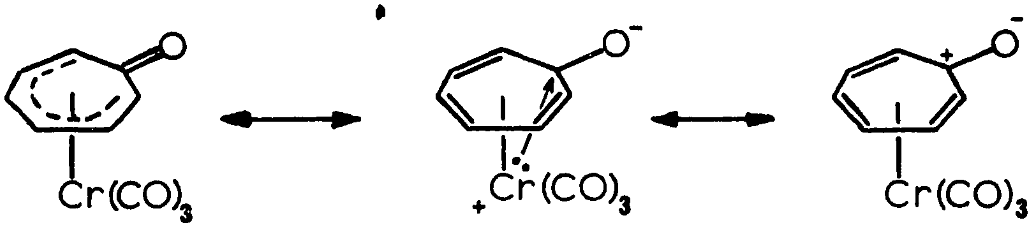
Pauson and Todd (34) have prepared (cycloheptatrienone)-tricarbonylchromium (18) from the reaction of (triacetonitrile)-tricarbonylchromium with cycloheptatrienone (tropone). The ketone moiety of 18 has been found to be similar in chemical reactivity to that of 15. The complex (18) has been protonated with hydrochloric acid to form the stable salt (19) analogous to 16. Alkylation of 18 has also been carried out using trialkyloxonium tetrafluoroborate; however, alkylation does not occur when poorer alkylating agents have been used (34).



The ketone moiety of 18 does not seem to be subject to nucleophilic attack. Complex 18 is essentially inert toward sodium borohydride, Grignard reagents, alkyl lithium reagents, 2,4-dinitrophenyl hydrazine and hydroxylamine.



Mills (35) has obtained the X-ray crystal structure of 18 and has found the tropone ring to be nonplanar. The carbon-oxygen double bond length is typically that of a carbonyl group at 1.23 Angstroms. The carbon-carbon bonds are unequal in length and the data favor resonance contributors 20 and 21 over 22. The resonance contributor 21 explains much of the chemistry associated with the ketone group of the complex. In the structure (21) the bond between the metal and C_1 of the

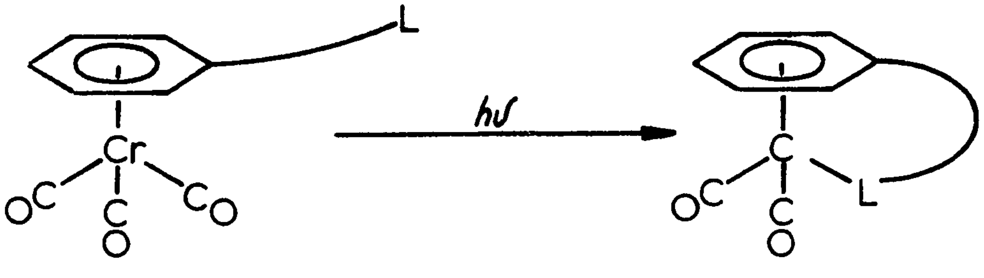


20 **21** **22**

tropone ring is formed by overlap of a *d* orbital of the metal and a vacant *p* orbital of the carbon atom of the polarized ketone group. The pair of electrons making the bond exists as an unshared pair on the metal in resonance structure **20**.

RESULTS

Several arene-tricarbonylchromium complexes were synthesized by standard methods (4,5) in which a functional group (L) was connected to the arene ring by a chain of atoms. Such compounds possess the general structure **23** and in many cases photolysis of **23** led to arene-chelate complexes (**24**). Other



23 **24**

arene-tricarbonylchromium complexes containing bicyclic organic arene ligands were synthesized in which a functional group is held juxtapositional to the tricarbonylchromium moiety. Photolysis of these complexes in some cases also led to arene-chelate complexes. Table II summarizes the arene-tricarbonylchromium complexes synthesized, the method of synthesis, the yield for each reaction and the carbonyl stretching frequency in the ir.

Characterization of (η^8-Benzobicyclo[2.2.1]heptadiene)-dicarbonylchromium

The reaction which produced (η^8-benzobicyclo[2.2.1]heptadiene)dicarbonylchromium (**25**) is representative of those reactions which led to arene-chelate complexes. Photolysis of a

Table II. Synthesis of arene-tricarbonylchromium complexes

Complexed arene ligand	Method of preparation	Yield (%)	$\nu(C\equiv O)$[a] (cm^{-1})	
Allyl phenyl ether	I[b]	34	1967	1900
Allyl 3-tolyl ether	I	25	1962	1894
Allyl 3,5-xylyl ether	I	30	1955	1889
Benzobicyclo[2.2.1]heptadiene	II[c]	35		1891[d]
Benzobicyclo[2.2.2]octadiene	II	32		1890[d]
Benzyl acrylate	-[e]	24	1968	1903
Benzyl vinyl ether	I	16	1968	1902
1,3-Diallyloxybenzene	I	37	1935	1898

---

[a] Solution ir in ether.

[b] Method I was the reaction of the arene ligands with hexacarbonylchromium in refluxing glyme-diglyme mixtures; see experimental section.

[c] Method II was the reaction of the arene ligands with (triacetonitrile)tricarbonylchromium; see experimental section.

[d] Some complexes exhibited very weak absorption in the region 1935 - 1970 cm^{-1} in ether but showed two very strong bands in other solvents.

[e] Prepared by the reaction of acroylyl chloride with (benzylalcohol)tricarbonylchromium.

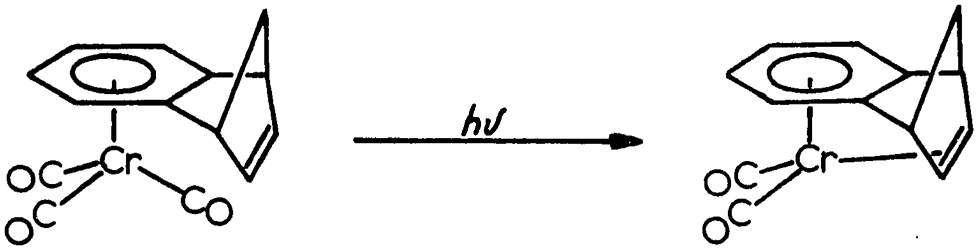
Table II. Continued

Complexed arene ligand	Method of Preparation	Yield (%)	$\nu(C{\equiv}O)^a$ (cm^{-1})	
Dibenzobicyclo[2.2.2]octatriene	II[f]	44		1890[d]
1,4-Dihydronaphthalene	II	20		1898[d]
4-Phenylbutene-1	I	76	1969	1901
4-Phenylbutylamine	III[g]	34	1965	1895
2-Phenylethylamine	III	13	1966	1897
6-Phenylhexene-1	I	23	1965	1900
5-Phenylpentene-1	I	32	1970	1902
3-Phenylpropene	I	24	1965	1892
3-Phenylpropylamine	III	36	1968	1898
1,3,5-Trihomoallylbenzene	I	17	1960	1895

[f] Prepared by Charles Baumann, see experimental section.

[g] Method III was the borane reduction of the corresponding nitrile arene-tricarbonylchromium complexes; see experimental section.

dilute ether solution of syn-(benzobicyclo[2.2.1]heptadiene)-tricarbonylchromium (26) yielded the arene-chelate complex (25).



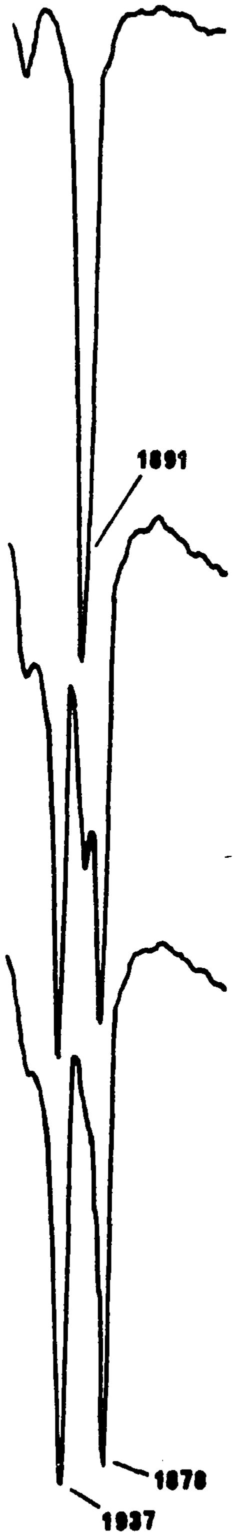
26 **25**

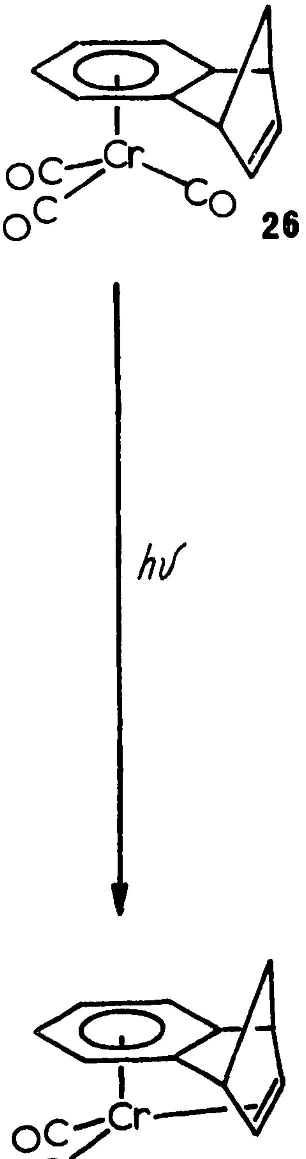
The reaction was accompanied by a color change from pale yellow to red-orange and was easily followed by changes in the carbonyl region of the ir spectrum with time. The ir change was a gradual decrease in the strong band of 26 at 1891 cm^{-1} with a corresponding development of the two strong bands of 25 at 1937 and 1878 cm^{-1}. The ir change is shown in Figure 1. The bands at 1937 and 1878 cm^{-1} which formed during the reaction exactly matched that of isolated, red crystalline 25.

The proton nmr spectrum of 25 (Figure 2) was similar to that of 26 (Figure 3) showing that the metal was still bound to the aromatic ring. The hydrogens of the etheno bridge of 25 were shifted about four ppm higher field than the hydrogens of the etheno bridge of 26, revealing that the etheno bridge of 25 was also bound to the metal.

The arene-chelate complex (25) was found to be monomeric by the osmometric molecular weight determination and by the mass spectrum. No evidence of dimer formation was found from

Figure 1. Infrared spectrum change in the photolysis of *syn*-(benzobicyclo[2.2.1]heptadiene)tricarbonylchromium in ether.



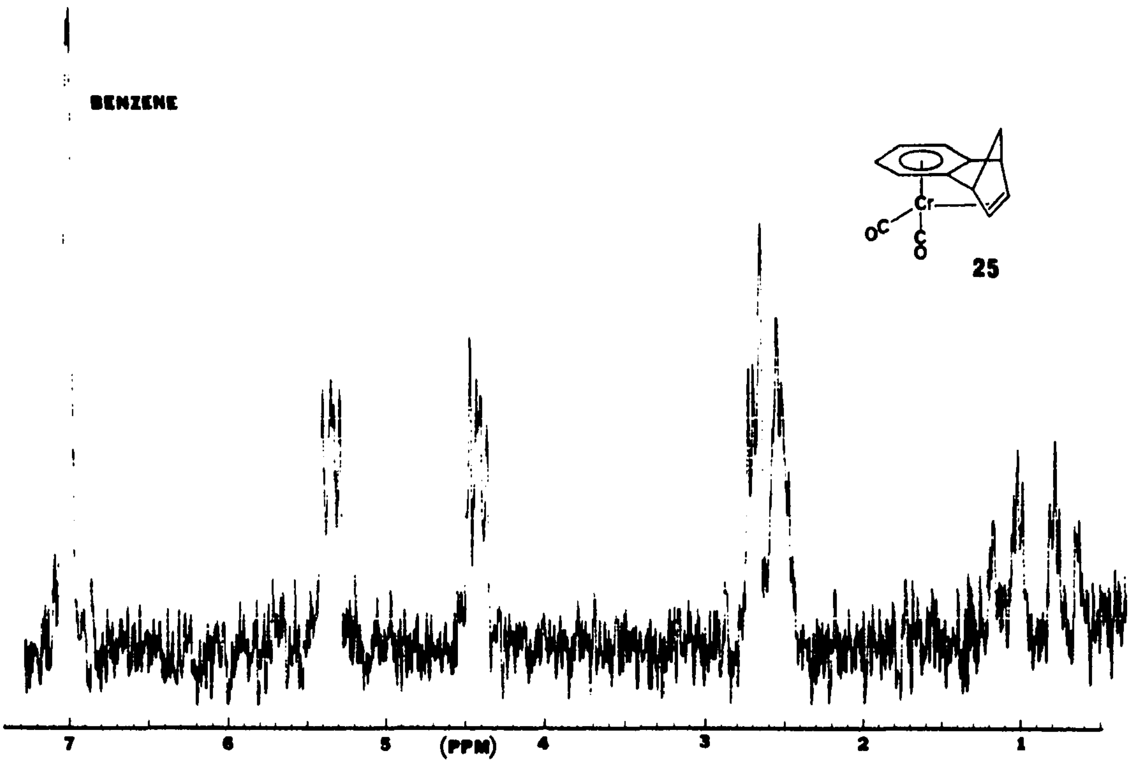


26

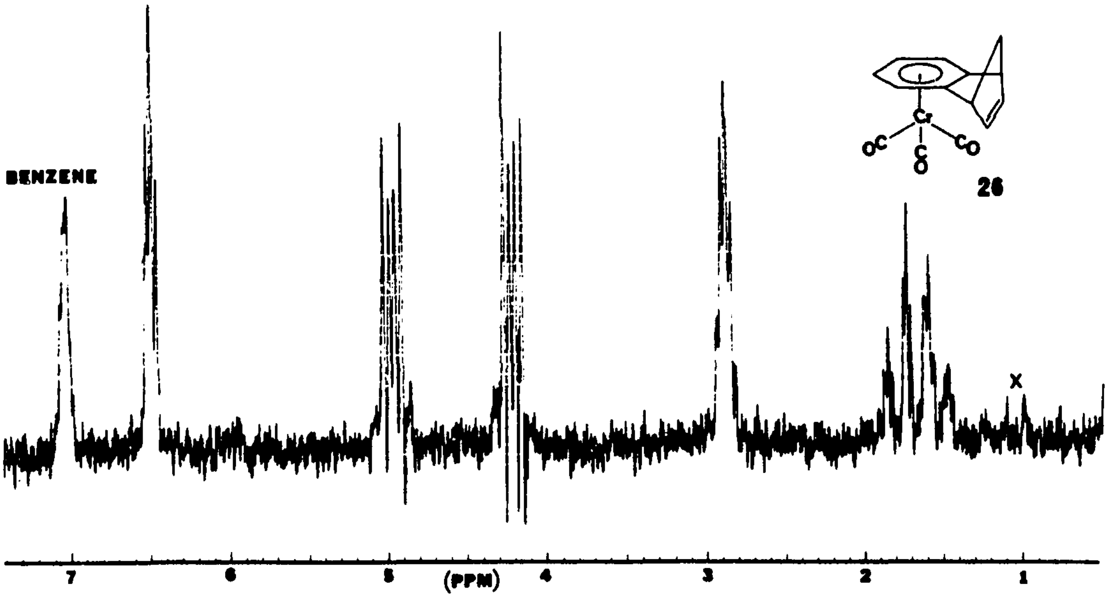
25

Figure 2. R-20B nmr spectrum of (η^8-benzobicyclo-[2.2.1]heptadiene)dicarbonylchromium in benzene-d_6.

Figure 3. R-20B nmr spectrum of *syn*-(benzobicyclo-[2.2.1]heptadiene)tricarbonylchromium in benzene-d_6.



25



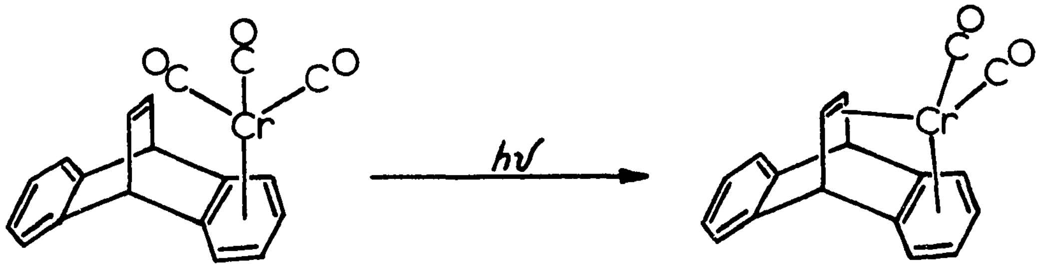
26

the mass spectroscopic data obtained for any of the arene-chelate complexes synthesized. The mass spectrum of **25** was consistent with the assigned structure, showing the correct parent ion and loss of two fragments of 28 units each.

The structure (**25**) was further confirmed by the fact that the free arene ligand benzobicyclo[2.2.1]heptadiene was removed intact in a 46% yield by the oxidative decomposition of **25** using cerium(IV).

Synthesis of Arene-chelate Complexes Containing Rigid Chelating-arene Ligands

The photoreactivity of *syn*-(dibenzobicyclo[2.2.2]octatriene)-tricarbonylchromium (**27**) was similar to that of *syn*-(benzobicyclo[2.2.1]heptadiene)tricarbonylchromium (**26**) in that the arene-chelate complex, **28**, was formed. The expected color change and ir change occurred, similar to that observed in the photoreaction of **26**.

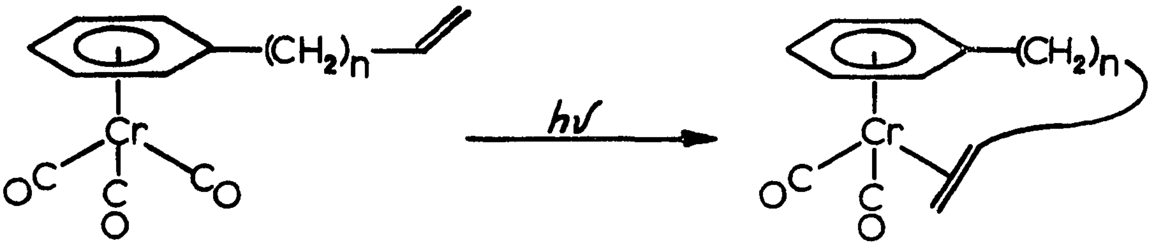


27 **28**

The photolysis reactions of *syn*-(benzobicyclo[2.2.2]octadiene)tricarbonylchromium (**29**) and (1,4-dihydronaphthalene)tricarbonylchromium (**30**) led to decomposition of the complexes and not to any stable arene-chelate complexes. Table III summarizes the results of the photolysis reactions of the arene-tricarbonylchromium complexes (**26**, **27**, **29** and **30**) containing rigid chelating-arene ligands benzobicyclo[2.2.1]heptadiene, dibenzobicyclo[2.2.2]octatriene, benzobicyclo[2.2.2]octadiene, and 1,4-dihydronaphthalene.

Synthesis of Arene-chelate Complexes from (Alkenylbenzene)tricarbonylchromium Precursors

Investigation of the photoreactivity of (3-phenylpropene)tricarbonylchromium (**31**), (4-phenylbutene-1)tricarbonylchromium (**32**), (5-phenylpentene-1)tricarbonylchromium (**33**), and (6-phenylhexene-1)tricarbonylchromium (**34**) was carried out. In the case of **31** a color change was observed during the photolysis, but no stable arene-chelate complex was isolated from the reaction. However, from the photoreactions of **32** and **33** stable arene-chelate complexes, (η^8-4-phenylbutene-1)dicarbonylchromium (**35**) and (η^8-5-phenylpentene-1)dicarbonylchromium (**36**)



32, n = 2
33, n = 3

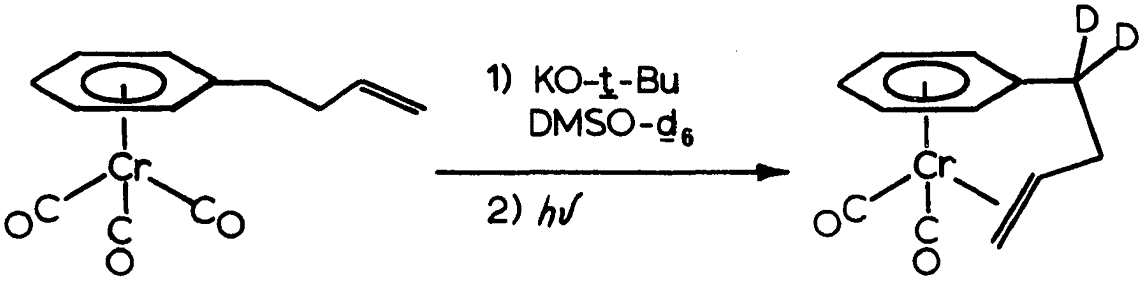
35, n = 2
36, n = 3

were isolated and characterized. In the photolysis of (6-phenylhexene-1)tricarbonylchromium (**34**) only decomposition was observed and no arene-chelate complex was isolated.

Table III. Photochemistry of arene-tricarbonylchromium complexes containing rigid chelating-arene ligands

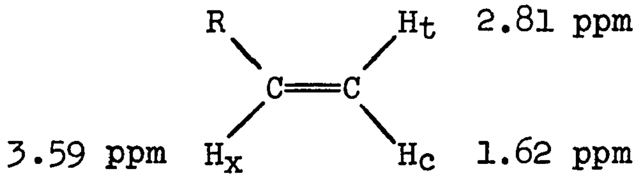
Tricarbonyl complex	Arene-chelate complex produced	Time of irradiation (min)	Final appearance of reaction mixture	Yield of arene-chelate complex (%)
26	**25**	65	red-orange	47
27	**28**	45	orange	55
29	None	60	colorless solution with grey-green precipitate	0
30	None	15	colorless solution with grey-green precipitate	0

In the characterization of (η^8-4-phenylbutene-1)dicarbonylchromium (**35**) the nmr spectrum obtained was complex. In order to make correct assignments a base-catalyzed hydrogen-deuterium exchange of the α-hydrogens of **32** was carried out followed by photolysis forming (η^8-α,α'-dideutero-4-phenylbutene-1)dicarbonylchromium (**37**).



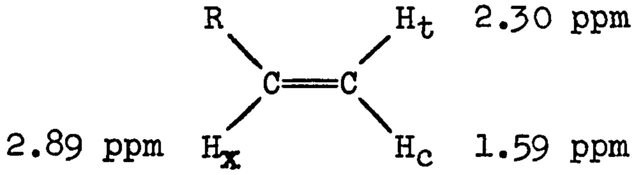
32 **37**

The nmr spectra of complexes 32, 35 and 37 are shown in Figures 4, 5 and 6 respectively. The assignment of the alkene hydrogens of 35 were made as shown.



$J_{ct} = 0$ Hz
$J_{cx} = 8.1$ Hz
$J_{tx} = 13.0$ Hz

The alkene hydrogens of (η^8-5-phenylpentene-1)dicarbonylchromium (36) had the following chemical shift values and coupling constants.



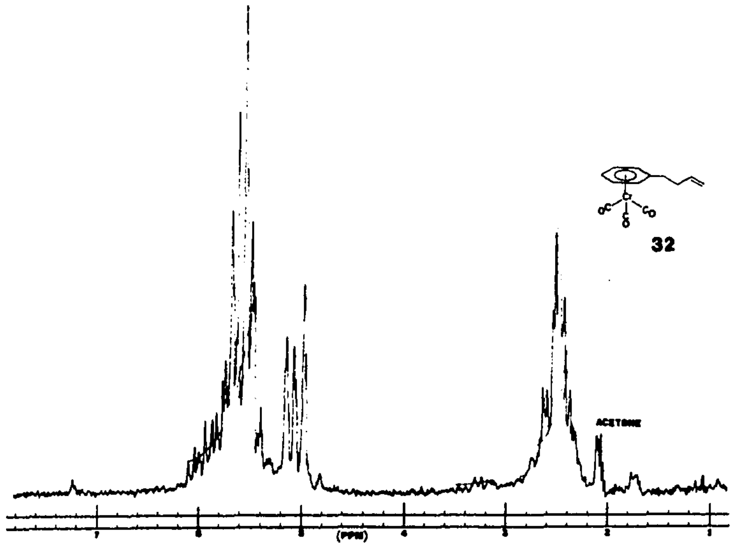
$J_{ct} = 0$ Hz
$J_{cx} = 8.3$ Hz
$J_{tx} = 13.1$ Hz

Table IV summarizes the results of the photoreactions of the (alkenylbenzene)tricarbonylchromium complexes (3-phenylpropene)tricarbonylchromium (31), (4-phenylbutene-1)tricarbonylchromium (32), (5-phenylpentene-1)tricarbonylchromium (33), and (6-phenylhexene-1)tricarbonylchromium (34).

Figure 4. HA-100 nmr spectrum of (4-phenylbutene-1)-tricarbonylchromium in acetone-$\underline{d}_6$.

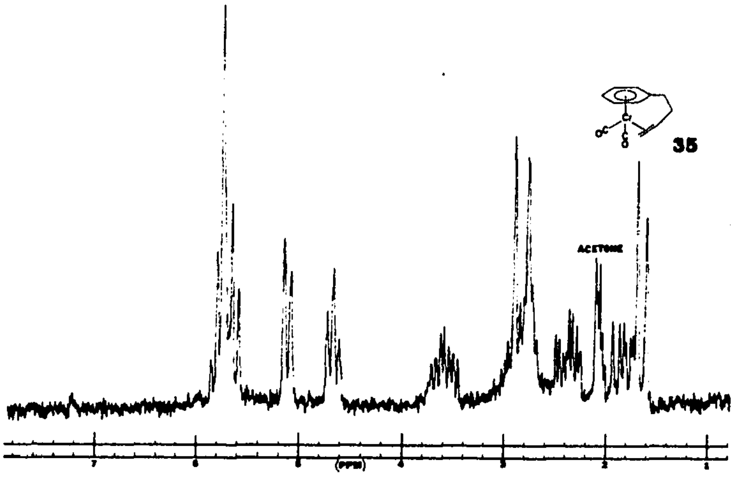
Figure 5. HA-100 nmr spectrum of (η^8-4-phenylbutene-1)dicarbonylchromium in acetone-$\underline{d}_6$.

Figure 6. HA-100 nmr spectrum of (η^8-α,α-dideutero-4-phenylbutene-1)dicarbonylchromium in acetone-$\underline{d}_6$.



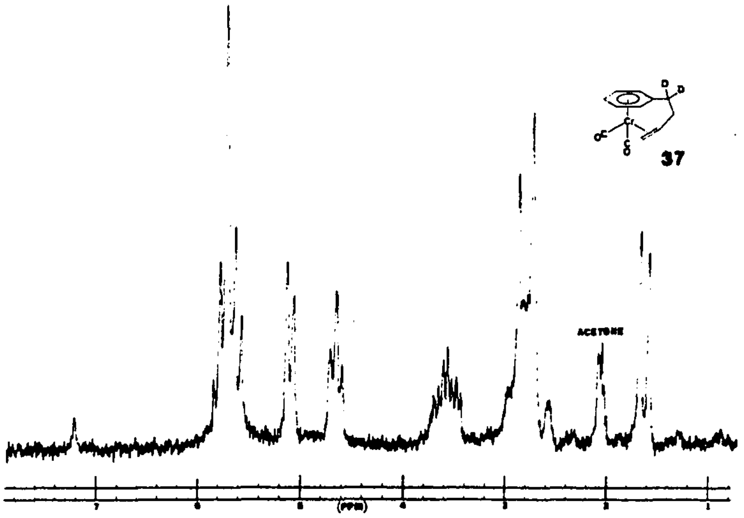
32

ACETONE
7
6
5
(PPM)
4
3
2
1



35

ACETONE
7
6
5
(PPM)
4
3
2
1



37

D
D
ACETONE
7
6
5
(PPM)
4
3
2
1

Table IV. Photochemistry of (alkenylbenzene)tricarbonylchromium complexes

Tricarbonyl complex	Arene-chelate complex isolated	Time of irradiation (min)	Final appearance of reaction mixture	Yield of arene-chelate complex (%)
31	None	a	turbid-orange	0
32	**35**	45	red-orange	53
33	**36**	70	turbid-orange	34
34	None	60	colorless with grey-green precipitate	0

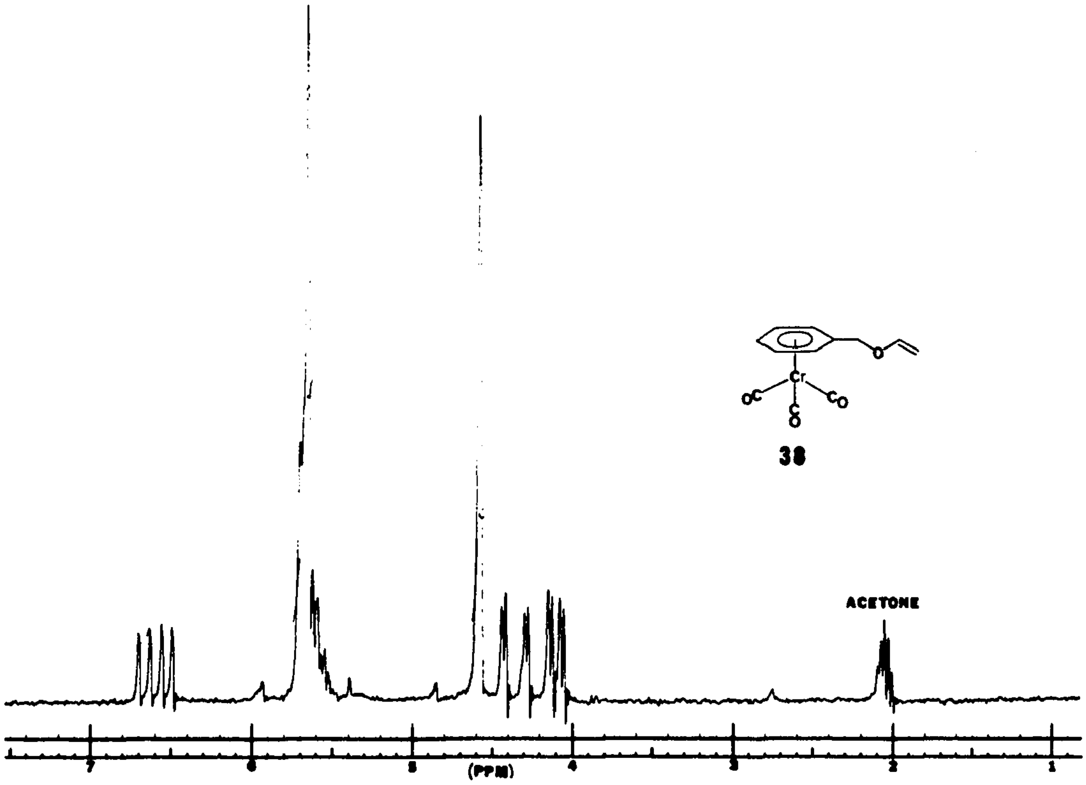
Synthesis of Arene-chelate Complexes from Chelating-arene Ligands Containing Ester or Ether Linkages

Arene-chelate complexes were formed from photolysis of (benzyl vinyl ether)tricarbonylchromium (**38**) and the tricarbonylchromium complexes of the allyl phenyl ether derivatives (allyl phenyl ether)tricarbonylchromium (**39**), (allyl 3-tolyl ether)tricarbonylchromium (**40**) and (allyl 3,5-xylyl ether)tricarbonylchromium (**41**). Photolysis of (benzyl acrylate)tricarbonylchromium (**42**) produced decomposition.

The nmr spectra of the tricarbonylchromium complexes **38**, **39**, **40** and **41** are shown in Figures 7, 8, 9 and 10 respectively.

Figure 7. HA-100 nmr spectrum of (benzyl vinyl ether)tricarbonylchromium in acetone-$\underline{d}_6$.

Figure 8. HA-100 nmr spectrum of (allyl phenyl ether)tricarbonylchromium in acetone-$\underline{d}_6$.


Cr
OC
CO
C
O
38
ACETONE
7
6
5
(PPM)
4
3
2
1

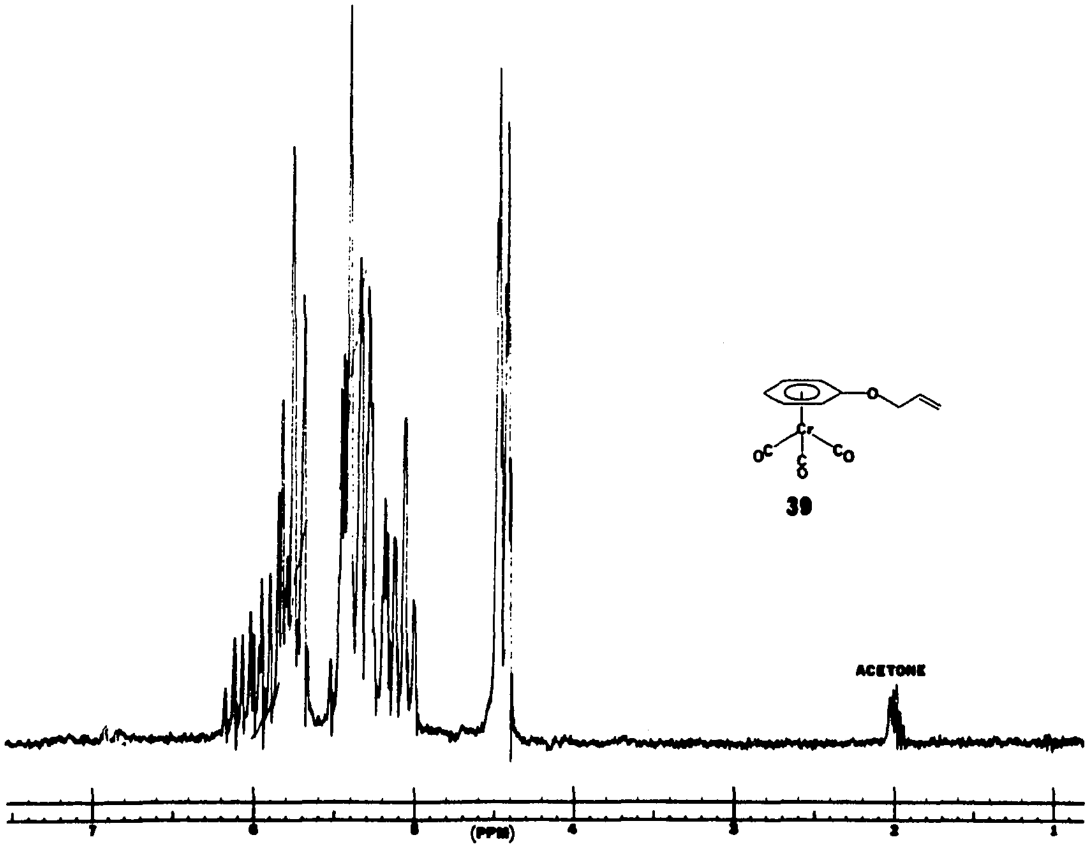
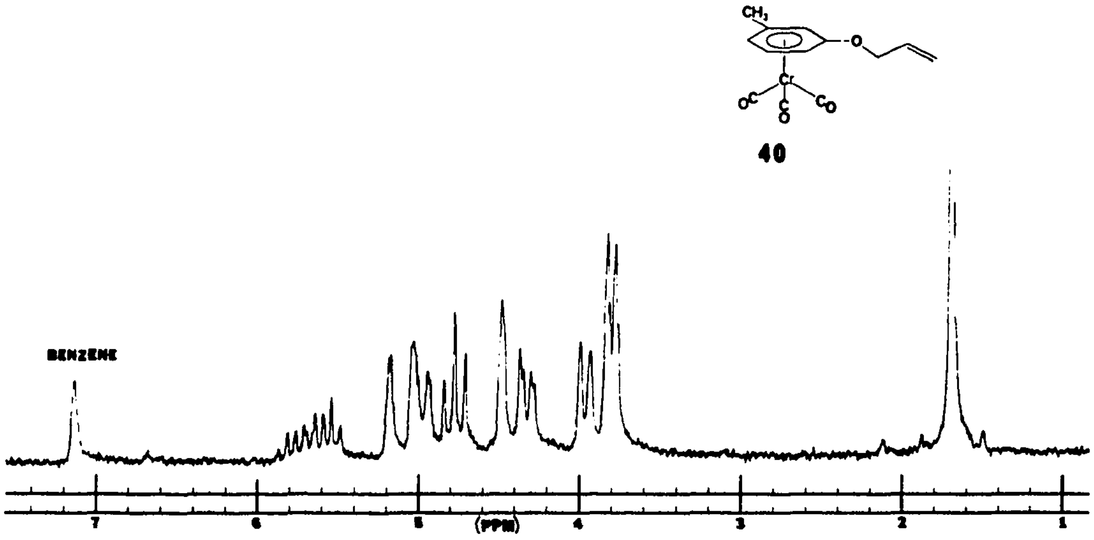

Cr
OC
CO
C
O
39
ACETONE
7
6
5
(PPM)
4
3
2
1

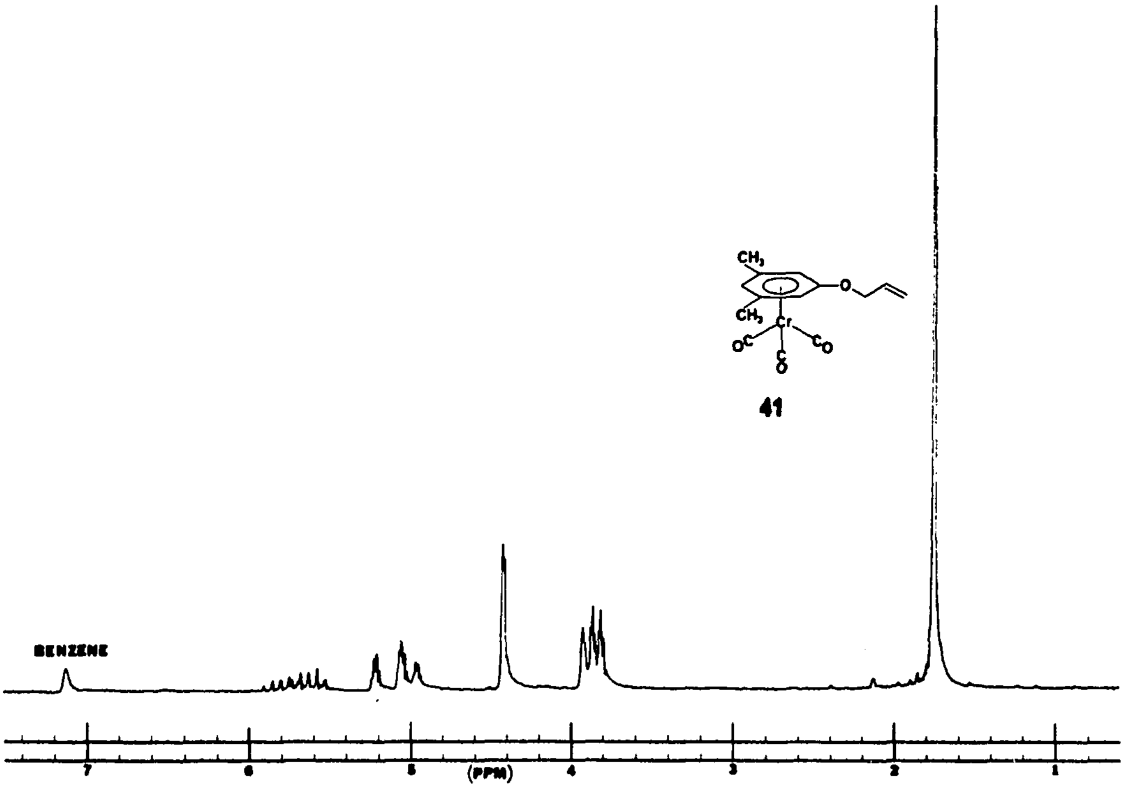
Figure 9. HA-100 nmr spectrum of (allyl 3-tolyl ether)tricarbonylchromium in benzene-$\underline{d}_6$.

Figure 10. HA-100 nmr spectrum of (allyl 3,5-xylyl ether)tricarbonylchromium in benzene-$\underline{d}_6$.



40

CH₃
O
Cr
OC
CO
C
O
BENZENE
7
6
5
(PPM)
4
3
2
1



41

CH₃
CH₃
O
Cr
OC
CO
C
O
BENZENE
7
6
5
(PPM)
4
3
2
1

The nmr spectra of the arene-chelate complexes (η^8-allyl phenyl ether)dicarbonylchromium (43), (η^8-allyl 3-tolyl ether)-dicarbonylchromium (44) and (η^8-allyl 3,5-xylyl ether)dicarbonylchromium (45) are shown in Figures 11, 12 and 13 respectively. An acceptable nmr spectrum was not obtained of the arene-chelate complex (benzyl vinyl ether)dicarbonylchromium (46) which formed in the photolysis of (benzyl vinyl ether)tricarbonylchromium (38).

The nmr spectrum of (η^8-allyl 3-tolyl ether)dicarbonyl-chromium (44) shows the mixture of the two diasteroisomers (47 and 48) produced in the photolysis of (allyl 3-tolyl ether)tricarbonylchromium (40).

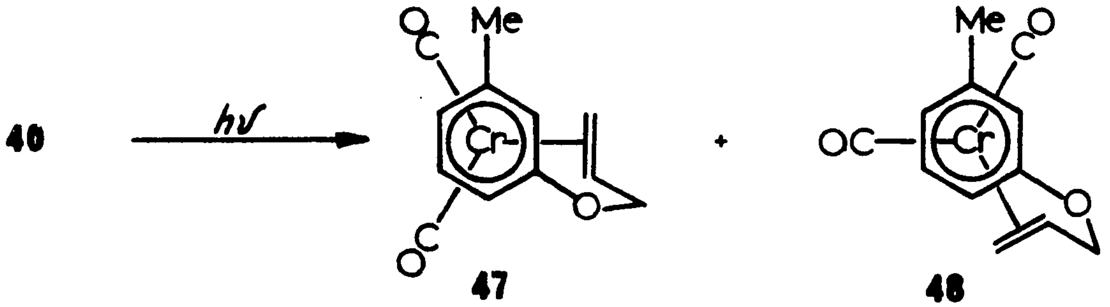
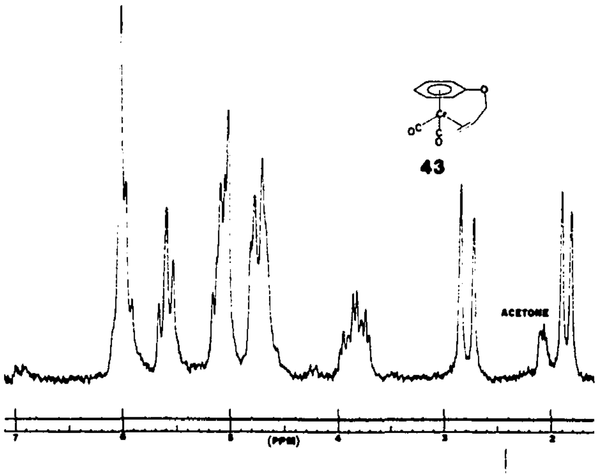


Table V summarizes the data of the photoreactions of (benzyl vinyl ether)tricarbonylchromium (38), (allyl phenyl ether)tricarbonylchromium (39), (allyl 3-tolyl ether)tricarbonylchromium (40), (allyl 3,5-xylyl ether)tricarbonylchromium (41) and (benzyl acrylate)tricarbonylchromium (42).

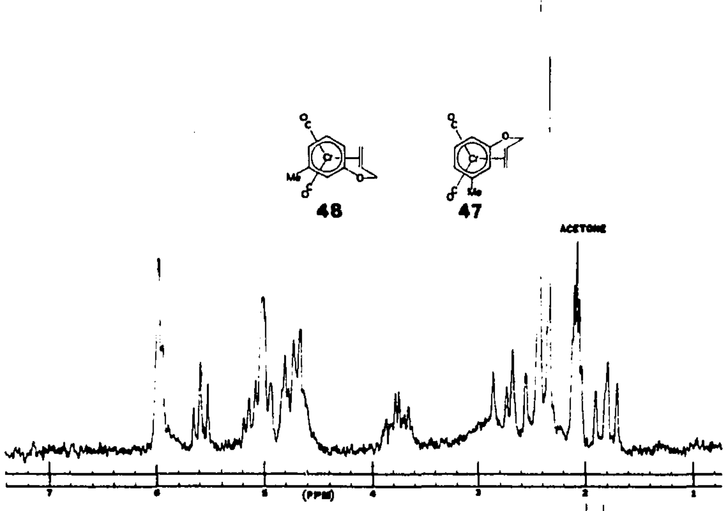
Figure 11. HA-100 nmr spectrum of (η^8-allyl phenyl ether)dicarbonylchromium in acetone-$\underline{d}_6$.

Figure 12. HA-100 nmr spectrum of the mixture of diastereomers of (η^8-allyl 3-tolyl ether)dicarbonylchromium in acetone-$\underline{d}_6$.

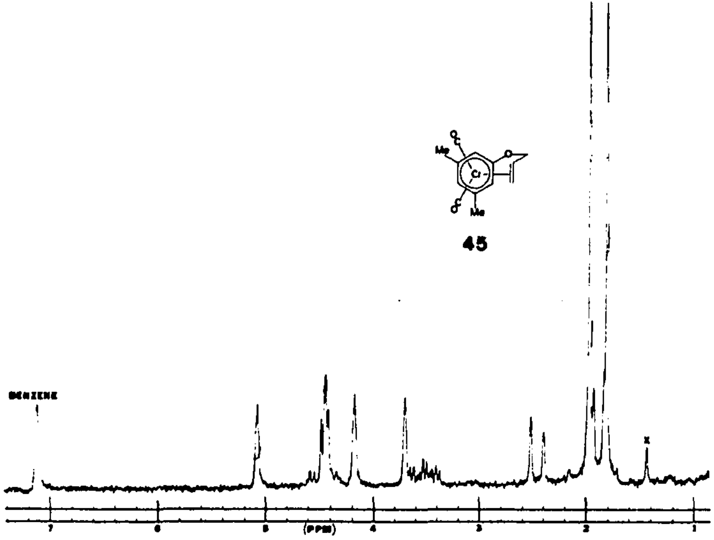
Figure 13. HA-100 nmr spectrum of (η^8-allyl 3,5-xylyl ether)dicarbonylchromium in benzene-$\underline{d}_6$.


43

ACETONE
OC
Cr
CO
O
7
6
5
(PPM)
4
3
2


48
47

Me
Cr
Me
ACETONE
7
6
5
(PPM)
4
3
2
1


45

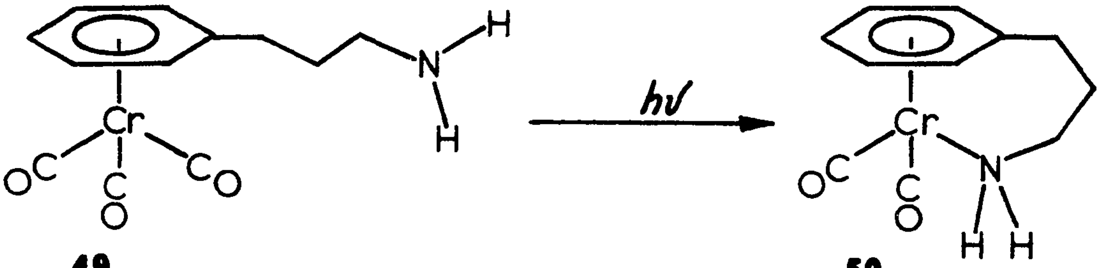
Me
Cr
Me
BENZENE
X
7
6
5
(PPM)
4
3
2
1

Table V. Photochemistry of (benzyl vinyl ether)tricarbonylchromium, (allyl phenyl ether)-tricarbonylchromium derivatives and (benzyl acrylate)tricarbonylchromium

Tricarbonyl complex	Arene-chelate complex produced	Time of irradiation (min)	Final appearance of reaction mixture	Yield of arene-chelate complex (%)
38	46	90	turbid-orange	17
39	43	105	dark orange	40
40	44	90	turbid-orange	48
41	45	105	turbid orange-yellow	47
42	None	60	colorless with grey-green precipitate	0

Synthesis of Arene-chelate Complexes from (Aminoalkylbenzene)tricarbonyl Precursors

The photoreaction of (3-phenylpropylamine)tricarbonylchromium (49) yielded the stable arene-chelate complex (3-phenylpropylamine)dicarbonylchromium (50). In the photol-



49 **50**

ysis of (2-phenylethylamine)tricarbonylchromium (51) a color change was observed along with a change in the carbonyl region of the ir spectrum consistent with the formation of (2-phenylethylamine)dicarbonylchromium (52); however, when the solvent was removed from the product mixture the red complex (52) decomposed leaving an insoluble grey-green material. (4-Phenylbutylamine)tricarbonylchromium (53) when photolyzed produced no color change and no evidence was noted for the formation of an arene-chelate complex in this reaction.

Table VI shows the pertinent data from the photoreactions of (3-phenylpropylamine)tricarbonylchromium (49), (2-phenylethylamine)tricarbonylchromium (51), and (4-phenylbutylamine)tricarbonylchromium (53).

Photochemistry of the Complexes (1,3-Diallyloxybenzene)tricarbonylchromium and (1,3,5-trihomoallylbenzene)-tricarbonylchromium

Irradiation of the tricarbonylchromium complexes of 1,3-diallyloxybenzene and 1,3,5-trihomoallylbenzene, 54 and 55 respectively, produced color changes and changes in the ir corresponding to the formation of the arene-chelate complexes 56 and 57. No evidence was noted for the formation of other

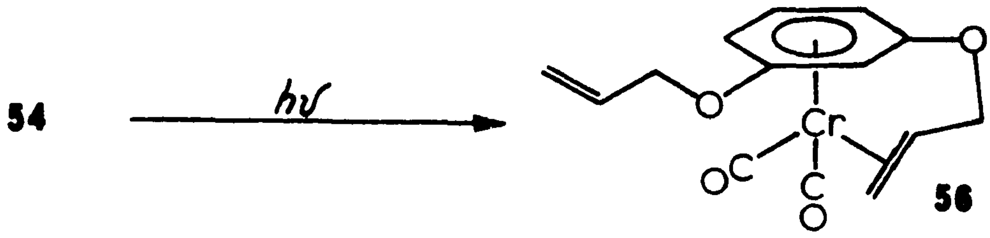
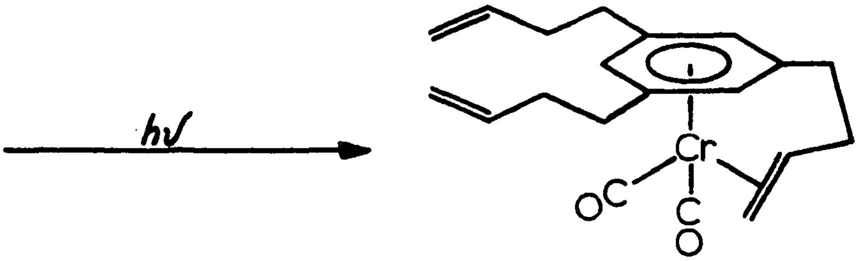


Table VI. Photochemistry of (aminoalkylbenzene)tricarbonylchromium complexes

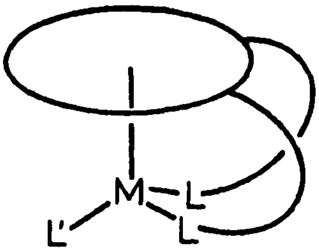
Tricarbonyl complex	Arene-chelate complex produced	Time of irradiation (min)	Final appearance of reaction mixture	Yield of arene-chelate produced (%)
49	50	45	red	39
51	52	25	red	0
53	None	15	colorless with grey-green precipitate	0

55

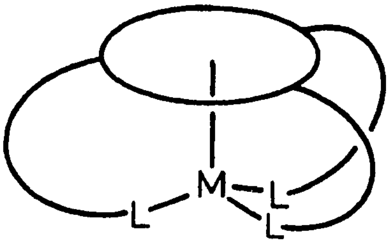


57

arene-chelate complexes fitting structures 13 or 14. Longer term irradiation led to decomposition of the complexes.



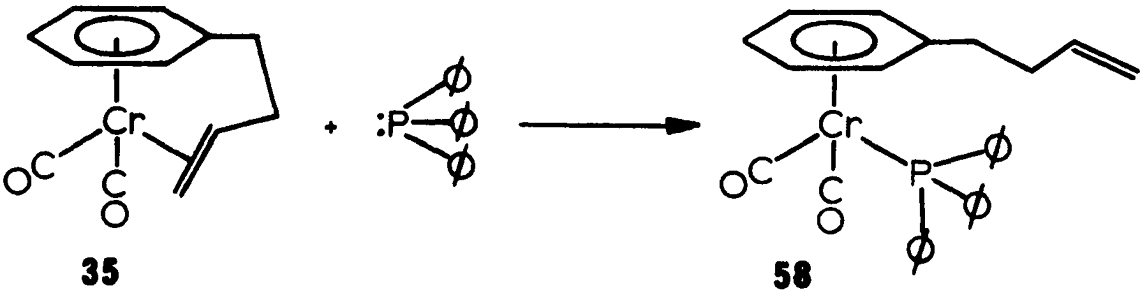
13



14

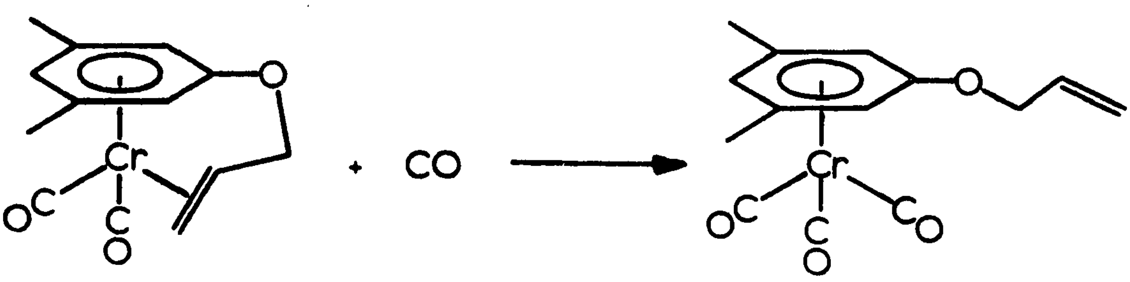
Reactivity of Arene-chelate Complexes

The chemical properties of (η^8-benzobicyclo[2.2.1]heptadiene)dicarbonylchromium (25) were studied by Howell (36). It was found that the metal-bound carbon-carbon double bond is displaced from the metal thermally by triphenylphosphine and other ligands. Similarly, the metal-bound carbon-carbon double bond of 35 was displaced by triphenylphosphine in a thermal reaction yielding (4-phenylbutene-1)(triphenylphosphine)dicarbonylchromium (58).



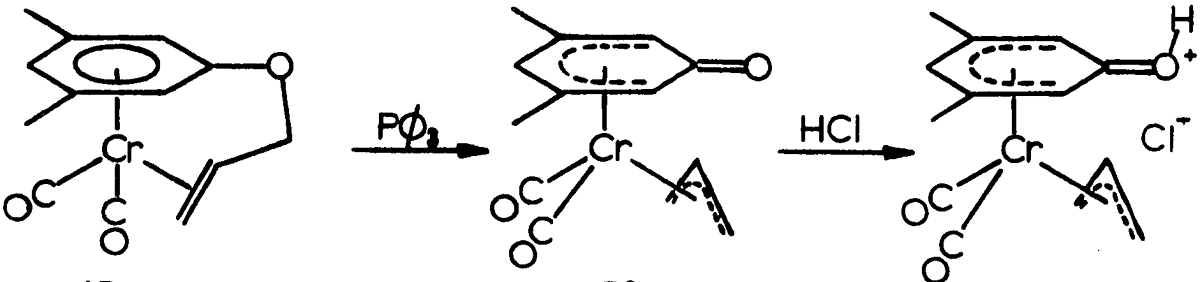
35 **58**

A displacement reaction also occurred when 45 was treated with carbon monoxide in benzene forming the tricarbonylchromium complex 41.



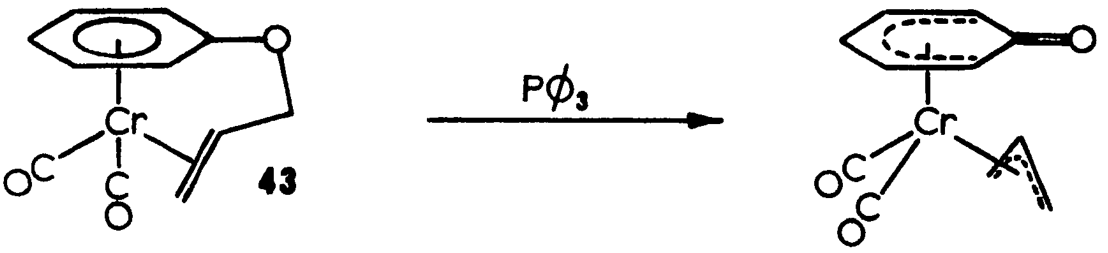
45 **41**

Treatment of 45 with triphenylphosphine did not give displacement of the carbon-carbon double bond from the metal as expected. Instead, a cleavage reaction occurred and (π-allyl)-(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) was isolated. The hydrochloride salt (60) which formed when 59 was treated with dry hydrochloric acid was also isolated and characterized. Complex 59 was also produced when triethylamine was substituted for triphenylphosphine in the reaction of 45.



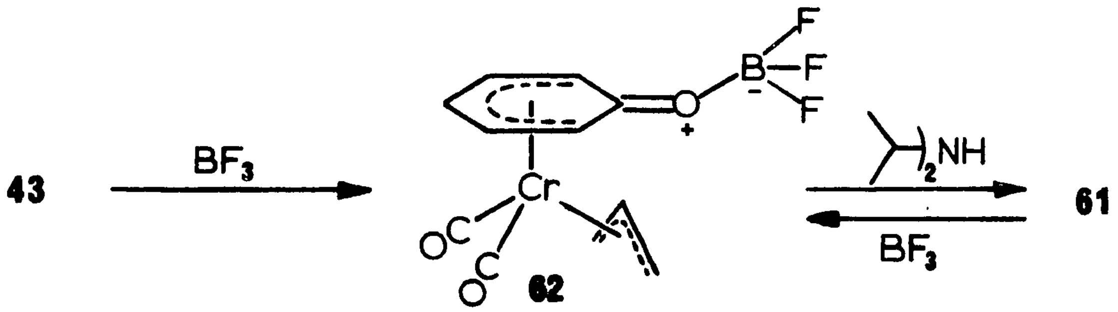
45 59 60

(η^8-Allyl phenyl ether)dicarbonylchromium (43) when treated with triphenylphosphine was analogous to 45 in reactivity and displacement of the metal-bound carbon-carbon double bond did not occur. The cleavage product (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) was formed in a fair yield. The cleavage process also occurred forming the boron trifluoride



43 61

adduct (62) when boron trifluoride etherate was added to 43. The adduct (62) after isolation was then converted to 61 by addition of diisopropylamine. In a separate experiment the boron trifluoride adduct was obtained by treatment of 61 with boron trifluoride etherate.



The nmr spectra of the complexes 59, 61 and 62 are shown in Figures 14, 15 and 16 respectively.

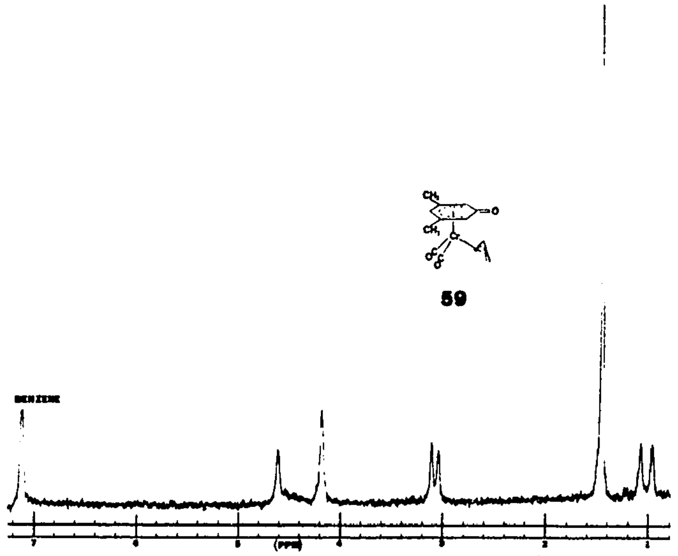
Table VII summarized some of the physical constants measured for the π-allyl, 6-oxocyclohexadienyl complexes synthesized.

The possibility of reaction of (π-allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) with nucleophiles and electrophiles was investigated. The complex (59) was found to be essentially inert to *n*-butyl lithium under the conditions investigated. Also, no alkylation occurred when 59 was treated with methyl iodide over a period of 18 hr.

Figure 14. HA-100 nmr spectrum of (π-allyl)-(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium in benzene-$\underline{d}_6$.

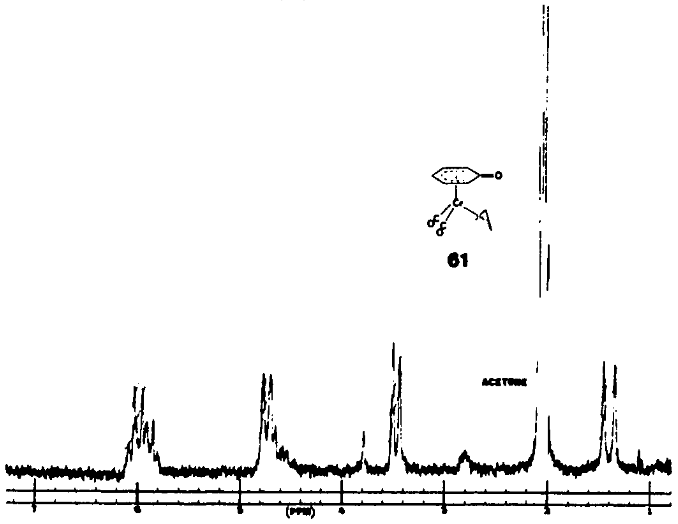
Figure 15. HA-100 nmr spectrum of (π-allyl)-(6-oxocyclohexadienyl)dicarbonylchromium in acetone-$\underline{d}_6$.

Figure 16. HA-100 nmr spectrum of the boron trifluoride adduct of (π-allyl)(6-oxocyclohexadienyl)-dicarbonylchromium in acetone-$\underline{d}_6$.



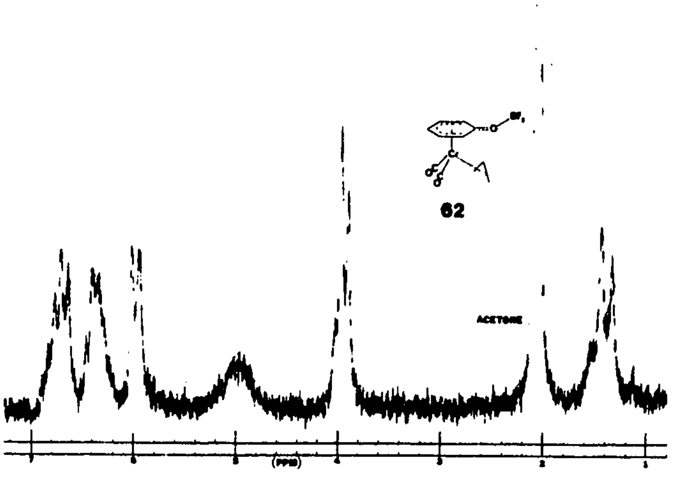
59

BENZENE
7
6
5
(PPM)
4
3
2
1



61

ACETONE
7
6
5
(PPM)
4
3
2
1



62

BF3
ACETONE
7
6
5
(PPM)
4
3
2
1

Table VII. Some physical constants of the (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium derivatives

		Infrared spectrum (cm^{-1})		Nmr spectrum (π-allyl A_2M_2X portion)					
Complex	mp(°C)[a]	ν(C≡O)	ν(C=O)	Proton assignments (ppm)			Coupling constants (Hz)		
				H_X	H_{M_2}	H_{A_2}	J_{AM}	J_{AX}	J_{MX}
59	110	1960, 1897[b]	1573	4.46	3.08	1.02[c]	~0	11.0	7.2
60	148	1976, 1922[d]	1551						
61	115	1957, 1899[e]	1597	4.61	3.46	1.39[f]	~0	12.0	7.0
62	140	1978, 1927[e]	1563	4.95	3.91	1.36[f]	~0	10.0	7.5

[a] Decomposition occurred at the indicated temperature.

[b] Chloroform was the solvent.

[c] Benzene-d_6 was the solvent.

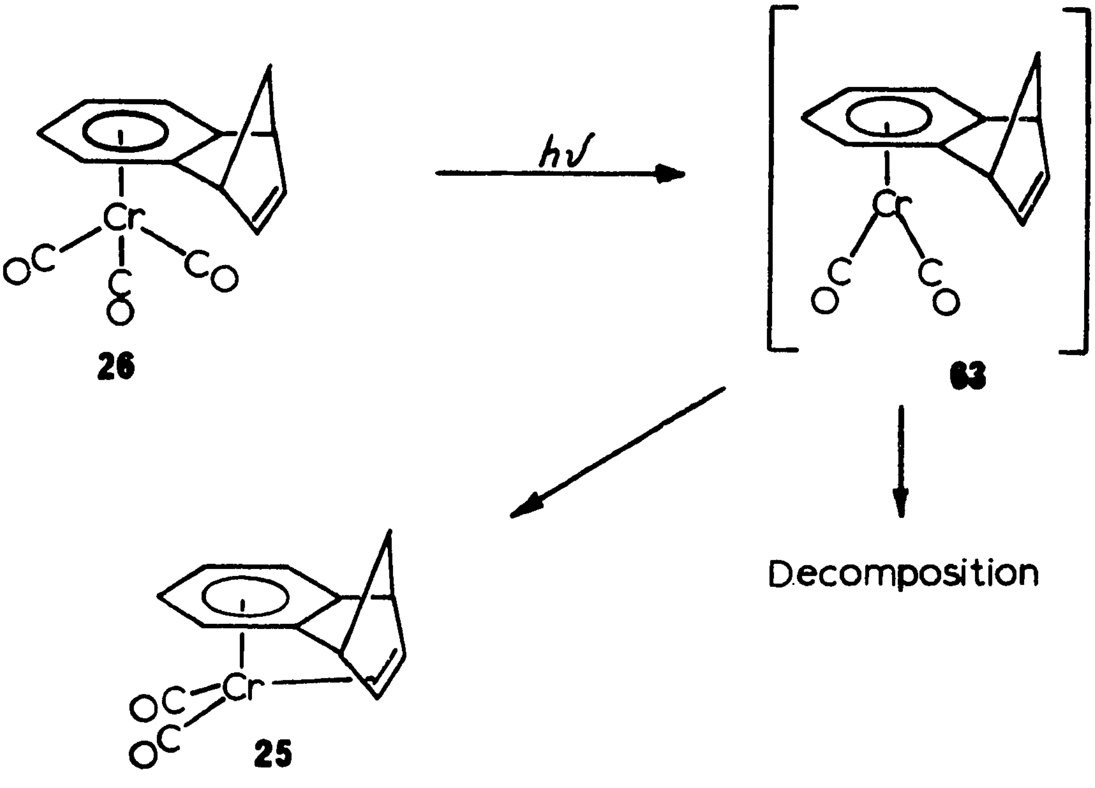
[d] KBr pellet.

[e] Tetrahydrofuran was the solvent.

[f] Acetone-d_6 was the solvent.

DISCUSSION

The formation of the arene-chelate complex **25** was possible because of the facile photoloss of a carbonyl from the corresponding arene-tricarbonylchromium complex. The photodecarbonylation reaction (17) leads to the co-ordinatively unsaturated chromium species **63** in the photolysis of **26**, which is free to decompose as well as form the arene-chelate complex (**25**). Some decomposition was observed in the photolysis of



26 and in the other photoreactions which led to arene-chelate complexes, suggesting that the co-ordinatively unsaturated chromium species has a life-time short enough that decomposition competes with chelate formation. Alternatively, 25 and the other arene-chelate complexes could be slightly photosensitive producing decomposition.

Both the ir and nmr spectra of 25 are consistent with the assigned structure. In comparing the ir spectrum of 26 to 25, the absorption of the carbonyls of the arene-chelate complex (25) is at lower energy than the carbonyl bands of the tricarbonylchromium complex (26). This is to be expected if a carbon-carbon double bond replaces a carbonyl, because the carbon-carbon double bond is less able to participitate in back bonding than the carbonyl (37). The proton nmr spectrum (Figure 2, page 20) and the carbon nmr (38) spectrum indicate that the carbon-carbon double bond is bound to the metal atom in the chelate structure (25). The chemical shift of the hydrogens of the etheno bridge of 25 is about 4.0 ppm higher field than the chemical shift of the hydrogens of the unbound etheno bridge of 26. The observation of the metal-bound carbon-carbon double bond at high field is consistent with that which has been observed in other systems where nmr spectra of π-complexed olefins have been measured (37).

Complexes of Rigid Chelating-arene Ligands

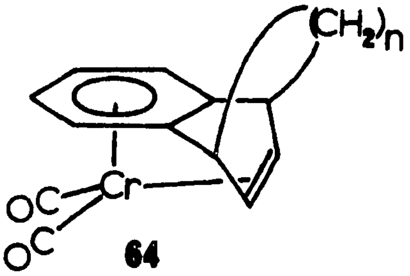
In view of the facile reaction of 26, producing the arene-chelate complex (25), the failure of *syn*-(benzobicyclo[2.2.2]-octadiene)tricarbonylchromium (29) to form an arene-chelate complex is unexpected. The result is inimical when one considers that (dibenzobicyclo[2.2.2]octatriene)dicarbonylchromium (**28**) is formed during the photolysis of the corresponding arene-tricarbonylchromium complex (**27**).

Only subtle differences in the bicyclooctane framework exist between **27** and **29**; namely, difference in bond angles caused by varying the exo bridge--dimethano for **29** and benzo for **27**. Apparently, these slight changes in angles are enough to cause the reaction of **29** to fail.

The stereochemistry of **29** was assigned syn because of its mode of synthesis. Both **26** and **27** were synthesized from the reactions of the free arene ligands and (triacetonitrile)tricarbonylchromium with short reaction times (see experimental section) and produced exclusively the syn isomer in each case. In the preparation of **29** (synthesized under the same conditions as **26** and **27**) there was no indication of a mixture of isomers in the chromatography of the crude product and there is no reason to believe that the anti isomer was formed to any measurable extent.

In comparing (1,4-dihydronaphthalene)tricarbonylchromium (**30**) to **26**, **27** and **29** the naphthalene derivative has no bridge connecting the one and four positions. Thus, *a priori*, the carbon-carbon double bond of **30** is not held even as close to the tricarbonylchromium moiety as in complex **29** which failed to form an arene-chelate complex photochemically.

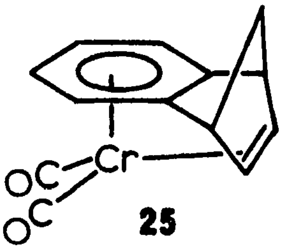
Arene-chelate complexes can be prepared, vide. supra., containing rigid chelating-arene ligands providing the carbon-carbon double bond is held close enough to the metal. In structure 64 the n=1 homolog is a very well-behaved complex and the n=0 homolog should also be stable. However, for homologs where the number of methylenes in the exo bridge is greater than one the complexes are not formed via the co-ordinatively unsaturated chromium species.



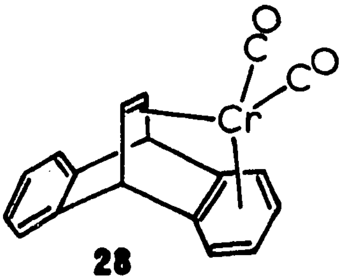
64

Chain Length Requirements

The arene-chelate complexes 25 and 28 have the carbon-carbon double bond moiety separated from the arene ring by one carbon atom. Because of the bicyclic nature of the chelating-

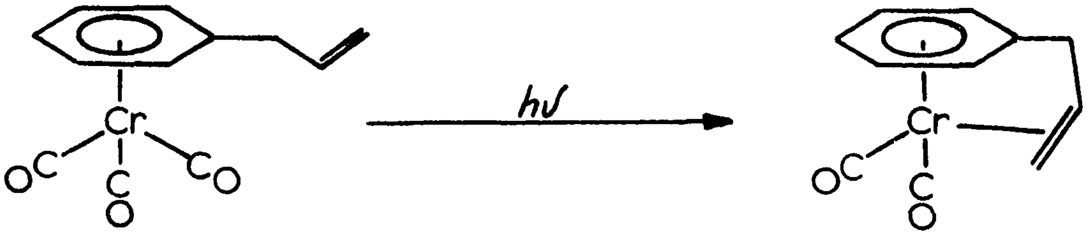


25



28

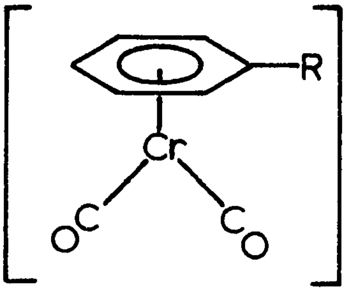
arene ligands of 25 and 28 the carbon-carbon double bond is held closer to the metal with less strain than in (3-phenylpropene)dicarbonylchromium (65). The complex (65) must have



31 65

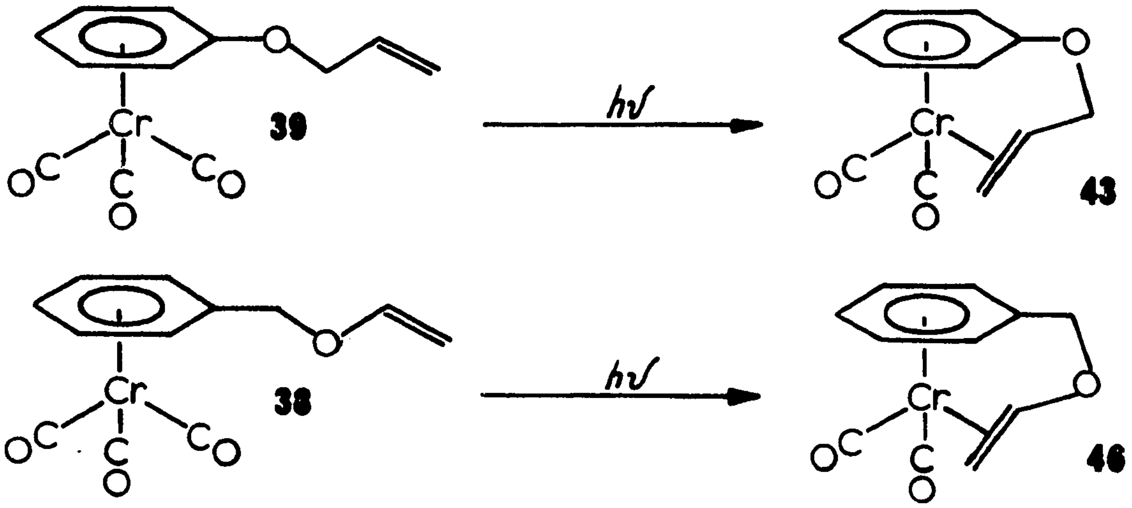
formed in the reaction of 31 since a color change occurred, whereas in the other photoreactions which failed to produce arene-chelate complexes no color change was observed. The color change is probably not a result of any intermolecular process or the photolysis of (6-phenylhexene-1)tricarbonylchromium (34) would have produced a color change. The apparent thermodynamic instability of 65 results from introduction of too much strain in the formation of 65 causing the complex to decompose. In the cases of 25 and 28 this strain is already built in and accounted for in the bicyclic chelating-arene ligands.

The results of the photolysis of the (alkenylbenzene)tricarbonylchromium complexes and the (aminoalkylbenzene)tricarbonylchromium complexes indicate that arene-chelate complexes form when the functional group (carbon-carbon double bond or amine) is connected to the arene ring by either two or three methylenes. A span of four methylenes separating the functional group from the arene ring makes the chain too long and the co-ordinatively unsaturated chromium species (2) decomposes before the functional group can bond to the metal, forming the chelate.



2

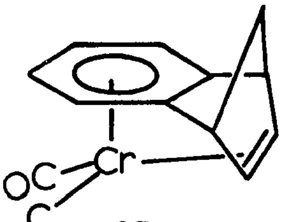
The chain of atoms separating the functional group and the arene ring in the arene-tricarbonylchromium complexes can be an oxygen atom and a methylene in either order and form the chelate during photolysis. This is shown by the formation of the allyl phenyl ether and benzyl vinyl ether chelate complexes (43 and 46) from the photoreactions of 39 and 38. Experimen-



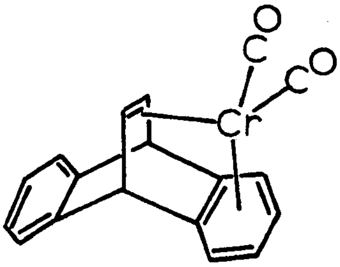
tally, it has not been determined whether other heteroatoms could be used successfully in place of the oxygen atom. (Allylphenylamine)tricarbonylchromium should form a stable arene-chelate complex.

Orientation of the Carbon-carbon Double Bond in Arene-chelate Complexes

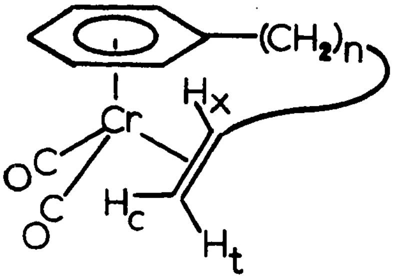
In the bicyclic ligands of the arene-chelate complexes (25 and 28) the metal-bound carbon-carbon double bond must be parallel to the arene ring. The arene-chelate complexes such as 35 and 36, where the carbon-carbon double bond is attached to the arene ring by a flexible chain of atoms, there is some question as to whether the carbon-carbon double bond is parallel or perpendicular to the arene ring.



25



28



35, n = 2
36, n = 3

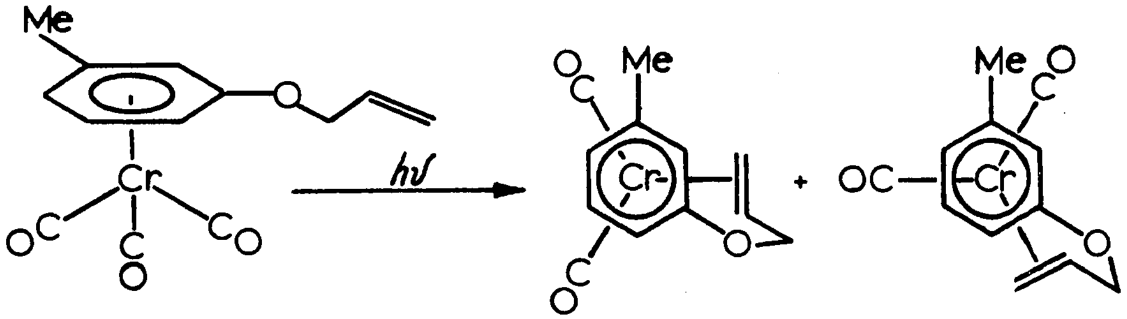
Assuming that the orientation is either parallel or perpendicular, the nmr spectral evidence supports the parallel orientation. For example, the nmr spectrum (Figure 5, page 26) of (4-phenylbutene-1)dicarbonylchromium (**35**) shows the terminal hydrogens (those bonded to C_1) to be much different from one another in chemical shift, 2.81 and 1.62 ppm. If the carbon-carbon double bond were perpendicular to the arene ring the protons on C_1 would be in more nearly the same magnetic environment and would thus have similar chemical shifts. The assignment of the orientation of the carbon-carbon double bond is equivocal since the hydrogens on C_1 would be in different magnetic environments in both the parallel and perpendicular orientations, and since the specific localized anisotropic effects of the metal are not clear.

The comparison of the nmr signals of the bound carbon-carbon double bond of **35** and the pentene chelate complex **36** shows similar chemical shifts and coupling constants, except for the chemical shifts of the hydrogen (H_X) on C_2 for each complex. For **35**, H_X is 3.59 ppm which is low field compared to H_X of **36** at 2.89 ppm. This suggests that H_X of **36** is closer to the metal atom than H_X of **35**, indicating that the pentene chain of **36** is perhaps more relaxed than the butene chain of **35**. Investigation of a good molecular model of **35** reveals that if the carbon-carbon double bond is roughly parallel to the arene ring, strain is introduced when both C_1 and C_2 are equidistant from the metal and the distance between the metal and the alkene carbons is maintained at the expected 2.33 angstroms (39).

The signals of the metal-bound carbon-carbon double bond can be seen clearly in the expanded high-field portion of the nmr spectrum of 43, Figure 17. The cis coupling ($J_{cx} = 9$ Hz) is less than the trans coupling ($J_{tx} = 13$ Hz). The chemical shift difference between H_t and H_c is also shown, further supporting the view that the carbon-carbon double bond is parallel to the arene ring.

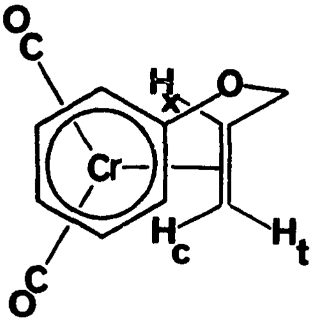
Chiral Nature of the Allyloxy Chain in the Allyl Phenyl Ether Arene-chelate Derivatives

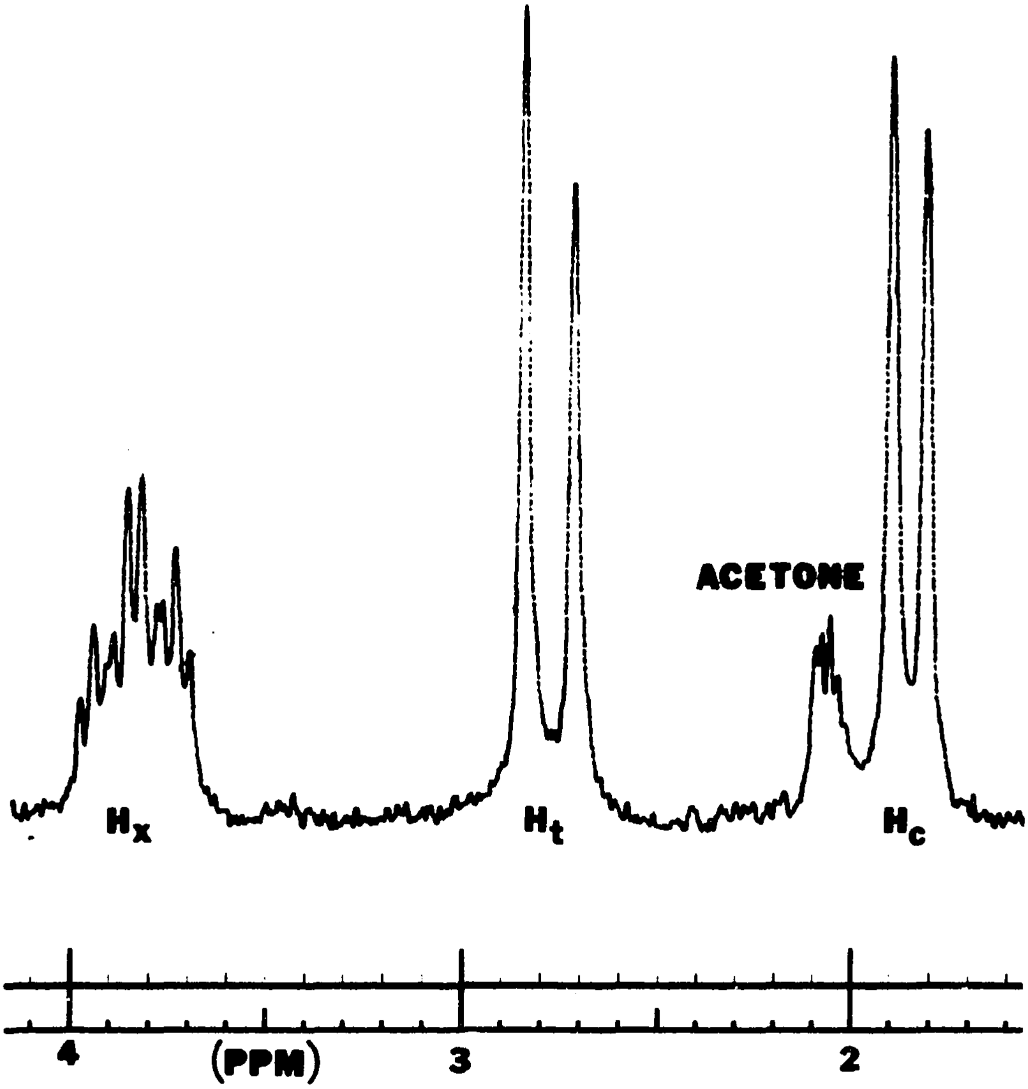
The allyloxy chain of the arene-chelate complex (allyl phenyl ether)dicarbonylchromium (43) is chiral. This has no consequence in the formation of 43 except to give an enantiomeric pair of isomers. However, in the photolysis of the asymmetric structure 40, two diastereomers are produced (47 and 48).



40 **47** **48**

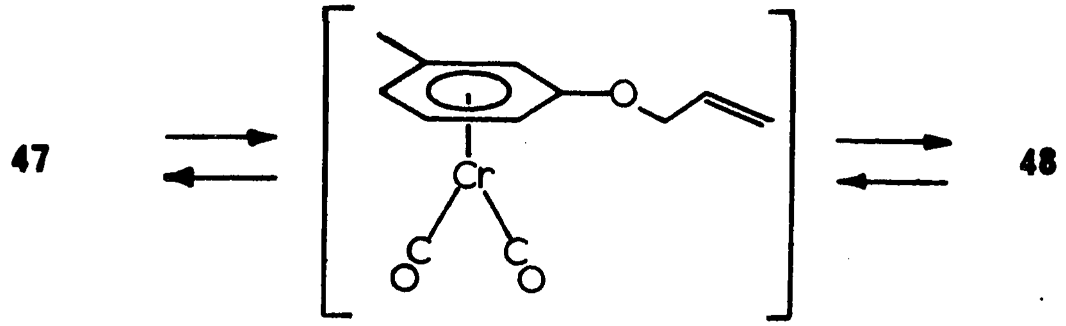
Figure 17. HA-100 nmr high-field signals of (η^6-allyl phenyl ether)dicarbonylchromium in acetone-$\underline{d}_6$.


OC
Cr
H_x
O
H_c
H_t
OC


ACETONE
H_x
H_t
H_c
4
(PPM)
3
2

The mixture of the diastereomers presents the nmr spectrum shown in Figure 12 (page 34). Examination of the spectrum reveals the methyl groups for 47 and 48 occur at different chemical shifts, 2.43 and 2.34 ppm. Also, there are two distinct sets of signals for the π-complexed carbon-carbon double bonds of each diastereomer. The nmr spectrum of the dimethyl analog, 45, (Figure 13, page 34) shows two nonequivalent diastereotopic methyl groups, indicating that no plane of symmetry exists in the molecule, and that the allyloxy chain is chiral.

The diastereomers, 47 and 48, are interconverted only if the carbon-carbon double bond is away from the metal long enough to change faces. The intermediate or species corresponding to the transition state for the process would essentially be the co-ordinatively unsaturated chromium species, 66. Even though the diastereomers (47 and 48) are observable by nmr, the above



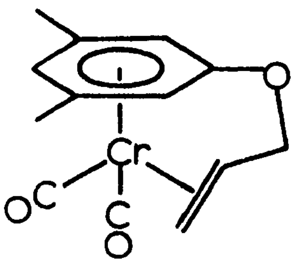
66

process could be occurring at a rapid rate. The diastereomers could not be separated by physical methods such as fractional crystallization, so that the facility of the interconversion of **47** and **48** remains enigmatic.

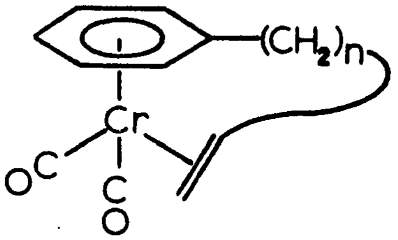
In olefin displacement reactions there is evidence that arene-dicarbonylchromium complexes containing olefin ligands undergo an equilibrium process, forming the co-ordinatively unsaturated chromium intermediate and liberating the olefin in solution (40). However, the process does not seem to be facile or explain the unreactivity of (hexamethylbenzene)-(maleic anhydride)dicarbonylchromium in the presence of triphenylphosphine in benzene at reflux (40).

Electronic Effects

On a qualitative basis the more electron rich the aromatic ring of the chelating-arene ligand the more stable the arene-chelate complex. For example, the allyl 3,5-xylyl ether arene-chelate complex (**45**) is stable in air at ambient temperature for long periods of time, whereas complexes **35** and **36** decompose in a few hours if not stored under nitrogen.



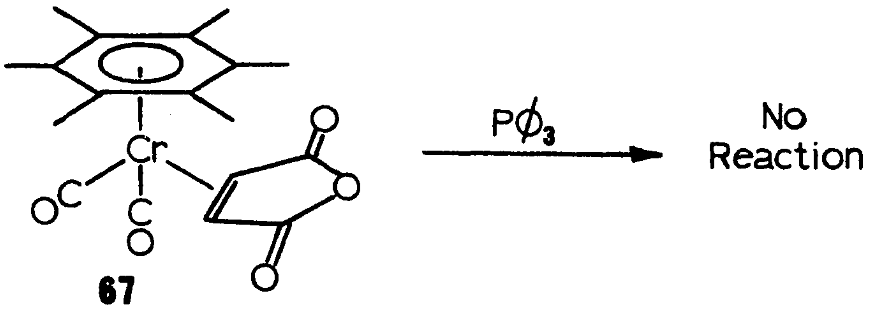
45



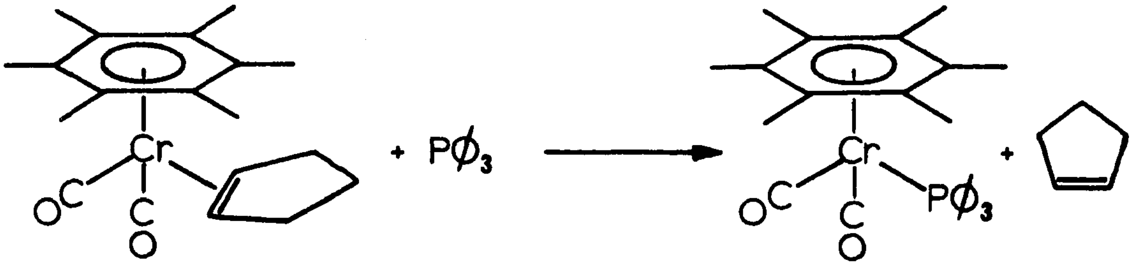
35, n = 2
36, n = 3

The result is in agreement with that found by Strohmeier (20) for nonchelated arene-dicarbonylchromium complexes with olefin ligands.

An electron withdrawing group attached to the carbon-carbon double bond of an olefin bonded to a metal stabilizes the complex. The maleic anhydride moiety in 67 is inert toward displacement by triphenylphosphine, even in benzene at reflux (40); whereas, cyclopentene is displaced rapidly and quantitatively from 68 at lower temperature (20). In order to investigate

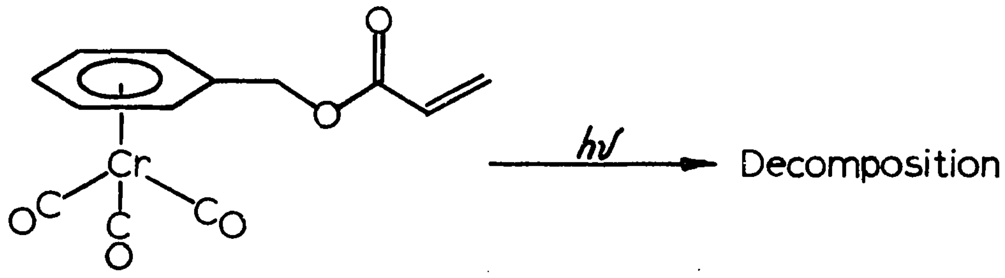


67



68

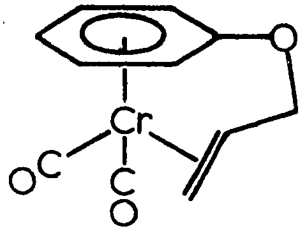
this electron withdrawing electronic effect in an arene-chelate system the benzyl acrylate arene-tricarbonylchromium complex (42) was synthesized. The photolysis of 42 failed to produce an arene-chelate complex and the decomposition of 42 was probably due to conformations of the acrylate moiety which disfavor chelation. The most stable conformations of the acrylate moiety are those where all atoms are coplanar, allowing conjugative interaction of the vinyl group with the carbonyl (41). The arene-chelate complex of benzyl acrylate would probably be stable indicating that the failure of 42 to form an arene-chelate complex is due to a kinetic problem. It is unclear what causes this kinetically unfavorable situation. A problem with chain length can be ruled out, since (5-phenylpentene-1)-tricarbonylchromium (33) formed an arene-chelate complex when irradiated. Possibly, the co-ordinatively unsaturated chromium species that forms when 42 is irradiated will not accept the carbon-carbon double bond when the acrylyl moiety is planar, but will accept only specific conformations (somewhere between s-cis and s-trans). This could serve to lower the rate of chelate formation enough that decomposition is favored.



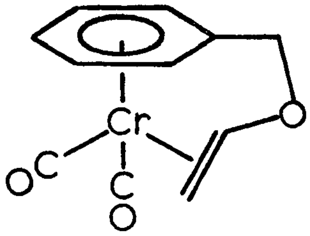
42

Electron donating groups attached to the carbon-carbon double bond of an olefin-metal complex cause destabilization.

The benzyl vinyl ether arene-chelate complex (46) is less stable than the isomeric allyl phenyl ether arene-chelate complex (43). Complex 46 was so sensitive that a good nmr



43

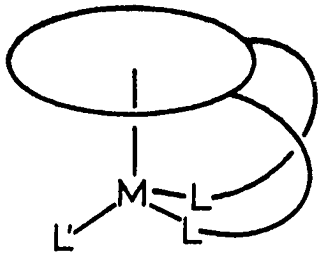


46

spectrum was not obtained; whereas, no problem of decomposition of 43 was encountered while in solution. The electronic effect of the oxygen atom is conjugative release into the olefin which causes the benzyl vinyl ether complex (46) to be labile compared to the allyl phenyl ether complex (43).

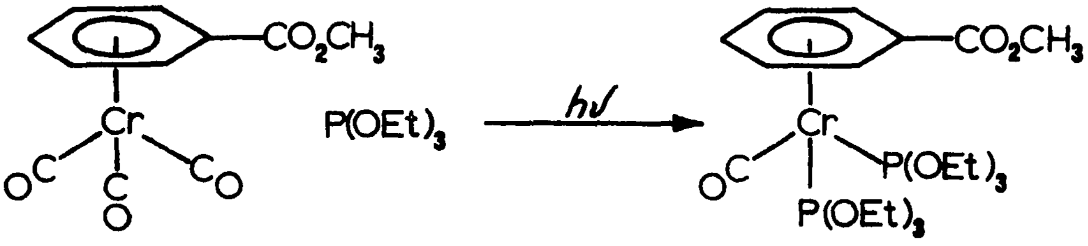
The More Novel Arene-chelate Complexes

Complexes resembling 13 were sought after but not observed in the photoreactions of (1,3-diallyloxybenzene)tricarbonylchromium (54) and (1,3,5-trihomoallylbenzene)tricarbonylchromium (55). In the photolysis of 54 (followed by ir) the spec-



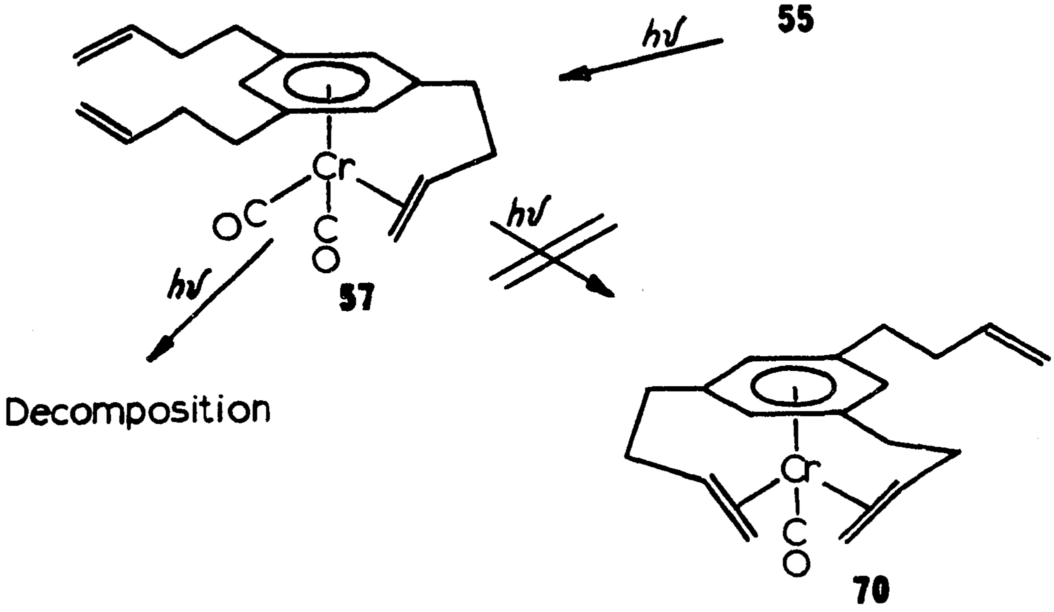
13

tral data suggest that only one of the allyloxy chains formed a bond to the metal. If both chains were connected to the metal by alkene-metal bonds, the ir spectrum would show development of a single band at about 1850 cm^{-1}. No such band was observed. From a symmetry argument an arene-monocarbonylchromium complex should have only one carbonyl band (11). The energy of the absorption of the carbonyl should be about 1850 cm^{-1} in the case of a monocarbonyl chelate structure if it is analogous to ir behavior of the known nonchelated arene-monocarbonylchromium complexes. For example, 69 has a single carbonyl absorption (excluding the ester carbonyl) at 1849 cm^{-1} (42).



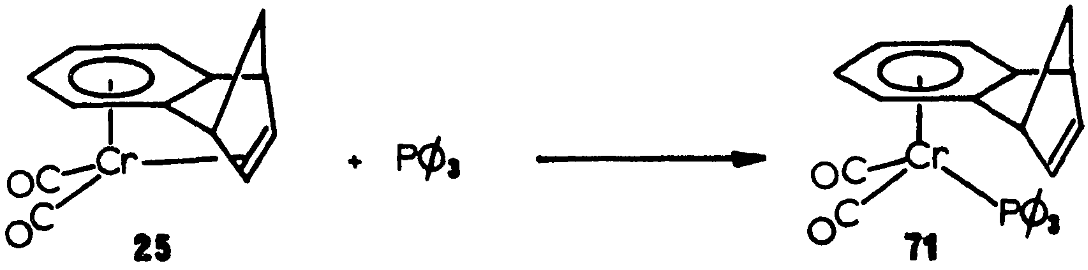
69

The photolysis of 55 did not yield any ir evidence for the formation of the chelate 70. Instead, decomposition was observed. The mode of decomposition is probably through photoloss of the carbon-carbon double bond from the metal of 57, reforming the co-ordinatively unsaturated chromium species which decomposes or reforms 57. Prolonged irradiation allows this process to repeat many times, eventually causing complete decomposition.



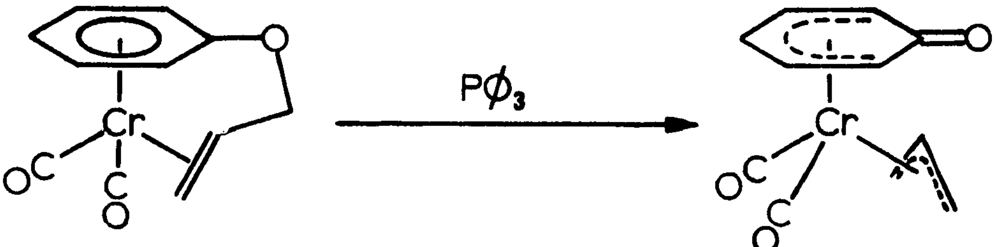
Reactions of Arene-chelate Complexes

The reaction of the arene-chelate complexes (η^8-benzobicyclo[2.2.1]heptadiene)dicarbonylchromium (25) and (η^8-4-phenylbutene-1)dicarbonylchromium (35) containing hydrocarbon chelating-arene ligands, with triphenylphosphine leads to displacement of the carbon-carbon double bond from the metal. For example, 71 is produced in 44 hours when 25 is mixed with triphenylphosphine in benzene at room temperature (36). The



complex (71) is the expected product from the reaction just as the displacement of the carbon-carbon double bond in the complex (η^8-allyl 3,5-xylyl ether)dicarbonylchromium (45) by carbon monoxide was anticipated, forming (allyl 3,5-xylyl ether)tricarbonylchromium (41).

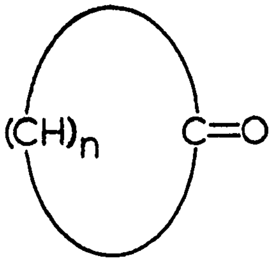
By contrast, reaction of 45 with triphenylphosphine gives the unexpected cleavage product, (π-allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59), which has been fully characterized. The parent complex (61) also forms from the reaction of the allyl phenyl ether arene-chelate complex (43) with triphenylphosphine. The reaction is unique in that π-allyl complexes have not been prepared in this way and a similar cleavage reaction of a metal complex has not appeared in the literature. The complex (61) is unique because it is the only chromium(0) organometallic complex reported to be appreciably soluble in water; and 61 is the only transition metal complex which houses the 6-oxocyclohexadienyl ligand.



43 **61**

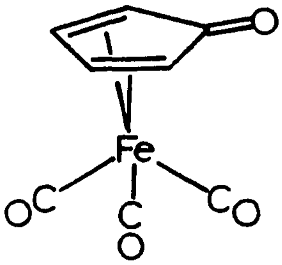
Viewing complex 61 as a 6-oxocyclohexadienyl complex, it belongs to the class of metal complexes containing the ligand

72. As a π-ligand 72 is well established in the n = 4, 5, and 6 homologs (cyclopentadienone)tricarbonyliron (15), the new

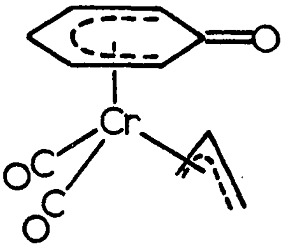


72

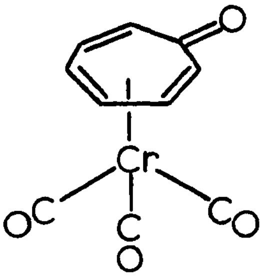
complex (61), and (cycloheptatrienone)tricarbonylchromium (18) respectively. Derivatives of the n = 3 homolog are known (43, 44). A derivative (73) has been listed as a



15

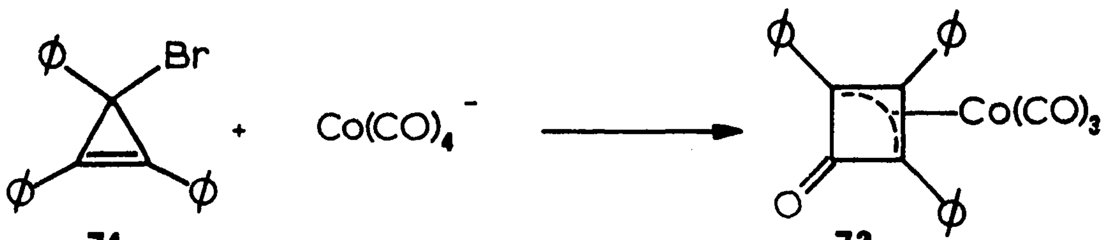


61



18

possible product from the reaction of 74 with tetracarbonylcobalt anion (44). The n = 2 homolog could probably be made from the known cyclopropenone (45) and a metal carbonyl.

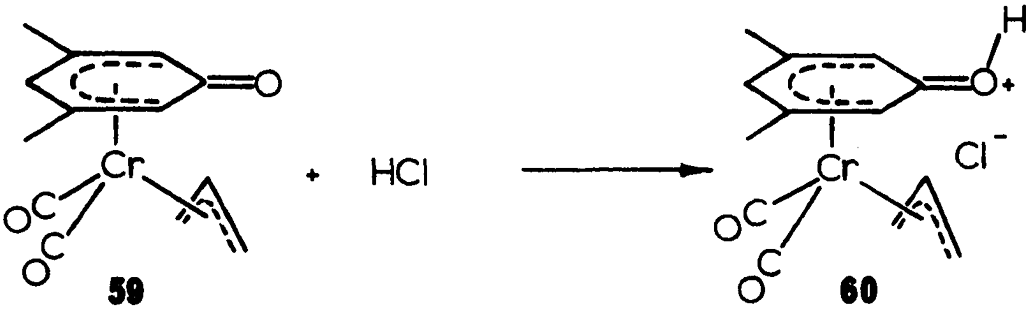


74

73

The chemistry associated with complexes containing ligands of structure 72 arises from the nature of the ketone moiety. The ketone behaves as if it has partial negative charge on the oxygen atom, but no partial positive charge at the carbon of the ketone center. All three complexes (15, 18 and 61) can be protonated by mineral acids (33, 34) forming stable salts, but neither 18 (34) nor 61 will accept nucleophilic attack on the ketone group. Methyl iodide will not alkylate either 18 (34) or 59, but triethyloxonium tetrafluoroborate ethylates the ketone group of the tropone derivative 18. The reaction of triethyloxonium tetrafluoroborate with the 6-oxocyclohexadienyl derivatives has not been investigated but should provide the ethylated analogs.

The protonated derivative (60) of 59 must still have double bond character in the ketone moiety as indicated by the slight shift in the ir to lower energy of the ketone group of 60 in tetrahydrofuran compared to that of 59 in the same solvent. The same result was observed in the protonation of the derivative 15, where the ketone of 15 absorbs at 1637 cm^{-1}.

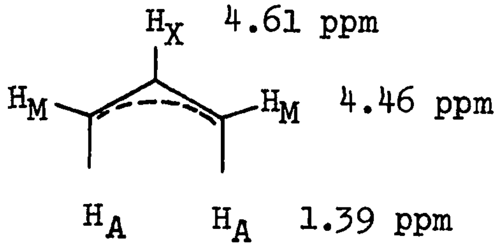


59

60

and the ketone of protonated 15 absorbs at 1527 cm^{-1} (33). The boron trifluoride adduct (62) of (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) also seems to have ample carbon-oxygen double bond character in the ketone group with its absorption at 1563 cm^{-1}.

The nmr spectra of the π-allyl, 6-oxocyclohexadienyl derivatives, Figures 14, 15 and 16 (page 42), show the A_2M_2X patterns for the π-allyl moieties for each complex. The following summarizes the chemical shifts and coupling constants for the hydrogens of the π-allyl ligand of (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61). These are consistent

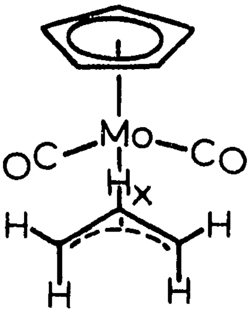


$J_{AX} = 12.0$ Hz

$J_{MX} = 7.0$ Hz

$J_{AM} \cong 0$ Hz

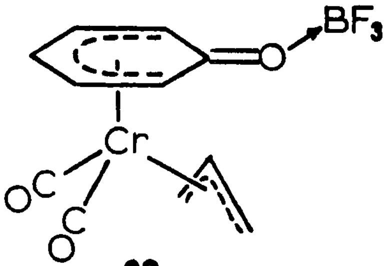
with nmr spectra of π-allyl complexes found in the literature. The closest analogy is the proton nmr study done on (π-allyl)-(cyclopentadienyl)dicarbonylmolybdenum (75), where the π-allyl, A_2M_2X portion of the spectrum is identical at 130° to that of 61 except for slight chemical shift differences (46, 47). At



75

lower temperature (less than 0°) two distinct conformations of the allyl moiety are observed. One conformation is heavily favored, but it is not clear which conformation is the major one (H_X pointing toward or away from the ring). The authors (47) believe that the conformation which has H_X pointing away from the ring is the most stable, although they give no reason for formulating this hypothesis.

The nmr spectrum of 62, the boron trifluoride adduct of 61, is similar to that of 61 except that the ring hydrogens of 62 are deshielded compared to those of 61. This is probably due to the electron withdrawing characteristics of the boron trifluoride moiety (48). In comparing the π-allyl portion of the nmr spectrum of (π-allyl)(6-oxocyclohexadienyl)dicarbonyl-

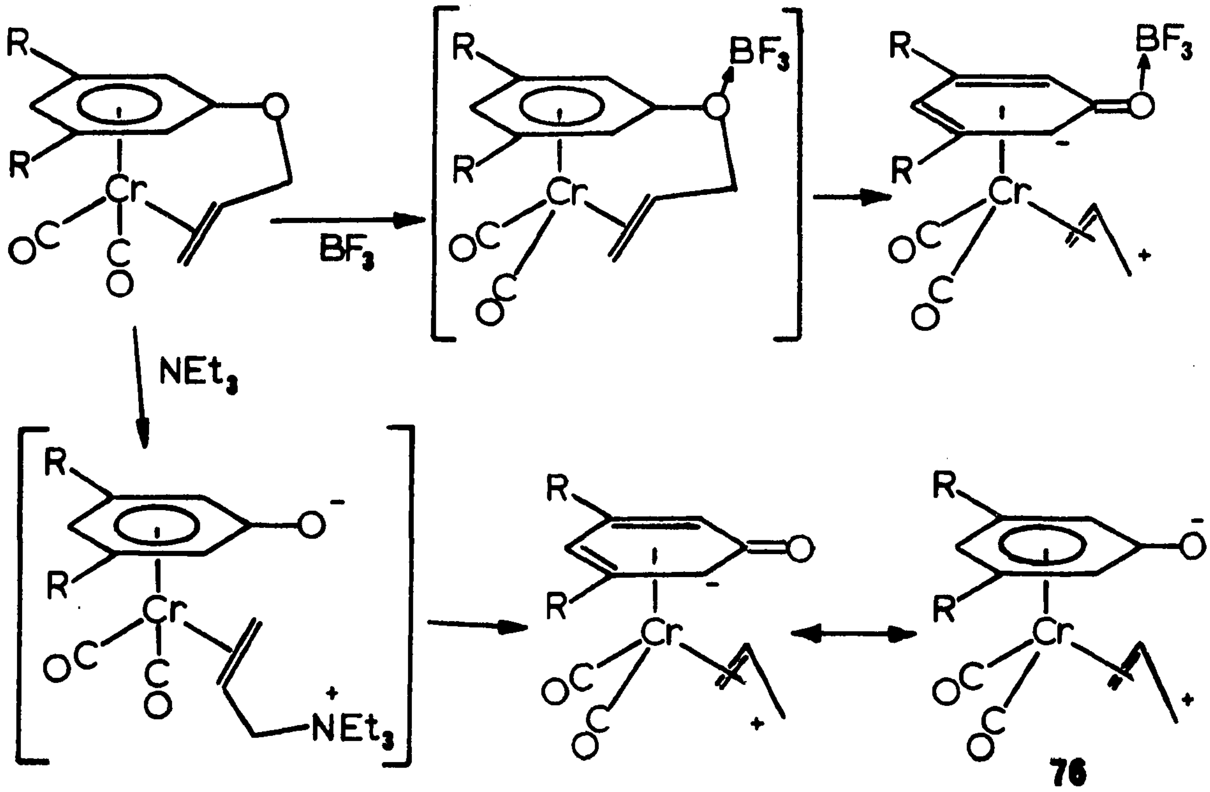


62

chromium (61) to that of the boron trifluoride adduct (62) of 61 (Table VII, page 44) the chemical shifts of H_M and H_X of 62 are lower field compared to the chemical shift of H_M and H_X of 61. The chemical shift of H_A for both complexes remains the same and is even a little lower field in the spectrum of 61. This perhaps indicates that the orentation of the π-bound allyl group is such that H_X is pointing toward the complexed ring of complexes 61 and 62, if the effect of the boron trifluoride moiety is to selectively deshield the protons on the π-allyl group which are closest to the boron trifluoride group.

Even though the conformation of the π-allyl group cannot be rigorously assigned in the π-allyl, 6-oxocyclohexadienyl system, it seems clear that only one conformer is favored at ambient temperature. The nmr spectrum of (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) remained unchanged at temperature as low as -50°. An nmr study at high temperature (> 31.4°) will have to be done to determine if the π-allyl group rotates and the rate of rotation. An X-ray analysis would also suggest the favored conformation of the π-allyl group.

The reaction of the allyl phenyl ether arene-chelate derivatives (43 and 45) forming the 6-oxocyclohexadienyl complexes is both Lewis acid and Lewis base catalyzed. The mechanism proposed for the reaction is shown as follows.

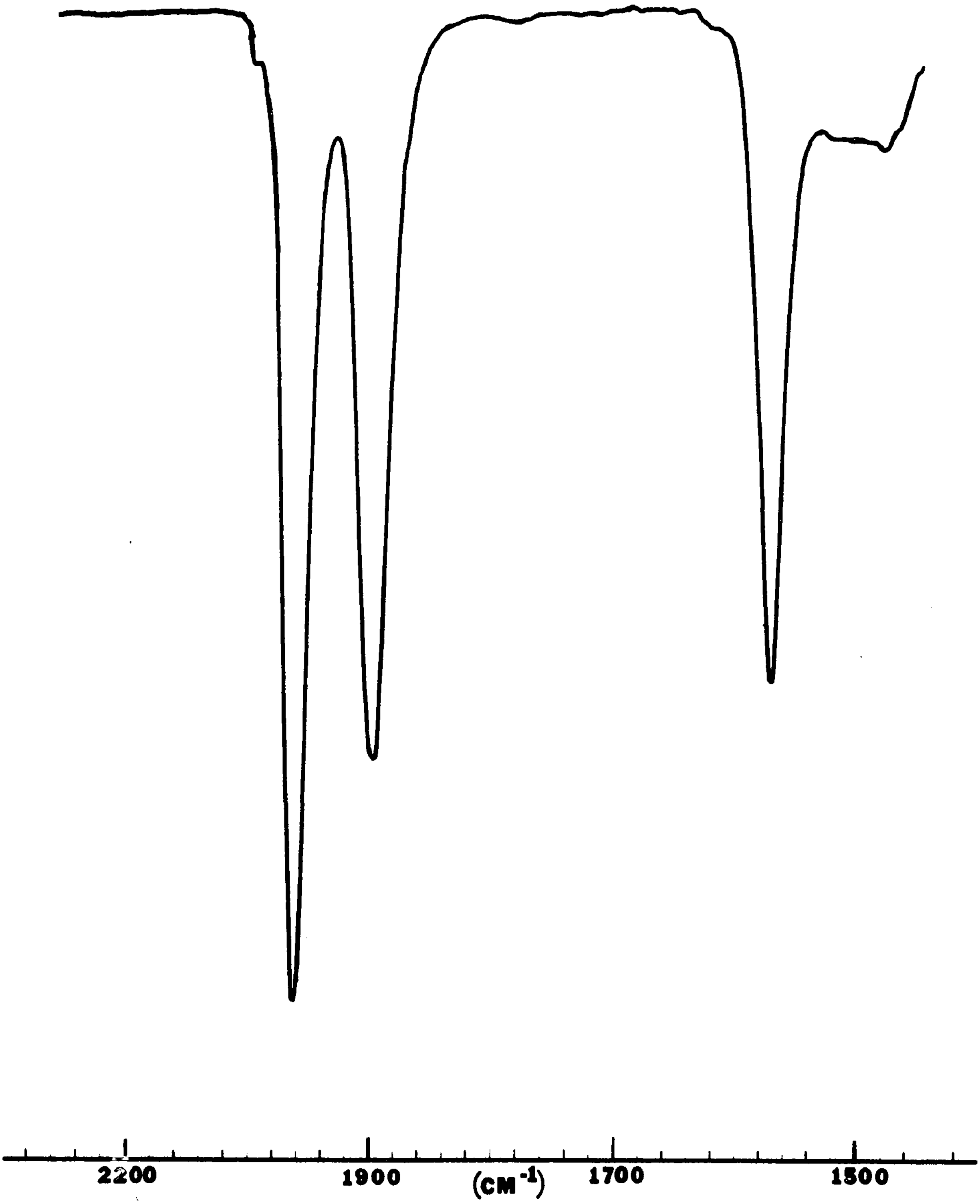


When triphenylphosphine is substituted for triethylamine in the above mechanism it is not clear which pathway is favored. Since tertiary phosphines are generally considered to be bases and more nucleophilic than amines (49), the triphenyl phosphine probably behaves as a nucleophile and attacks the metal-bound carbon-carbon double bond. Furthermore, the reaction of tertiary phosphines with olefins is well known and occurs readily when the carbon-carbon double bond of the olefin is electron deficient, forming quarternary phosphine intermediates which can be trapped with hydrogen halide (49, 50).

The proposed mechanism is, of course, not the only mechanism one could write for the process, but only a hypothesis which should be proved or disproved by experiment. The author believes that it could be established that triethylamine and triphenylphosphine attack the metal-bound carbon-carbon double bond by reaction of (η^8-allyl phenyl ether)dicarbonylchromium (43) with alkyl lithium. Perhaps alkylated intermediates could be detected or isolated lending credence to the mechanism envisaged.

The resonance contributor, 76, is believed to be responsible for much of the chemistry of the 6-oxocyclohexadienyl complexes and its zwitterionic character would also explain the water solubility of 59 and 61. The intensity of the carbon-oxygen double bond stretching vibration of 59 (Figure 18) at 1573 cm^{-1} is nearly that of the very strong absorption of the metal-bound carbonyls, showing the polar character of the ketone moiety. The ir spectrum of 59 in less polar solvent (carbon tetrachloride) shows the ketone absorption at 1597 cm^{-1}. This shift, due to the polar nature of the carbon-oxygen double bond, is in agreement with that observed by Pauson and Todd (34) for (tropone)tricarbonylchromium (18), where the ketone absorbs at 1623 cm^{-1} in acetonitrile and 1632 cm^{-1} in carbon tetrachloride.

Figure 18. IR-4250 infrared spectrum of (π-allyl)-(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium in chloroform.


2200
1900
(CM⁻¹)
1700
1500

EXPERIMENTAL

Equipment and Special Methods

Solvents used in chemical reactions except for benzene were distilled from calcium hydride prior to use. Benzene was dried by distillation after discarding the initial benzene-water azeotrope.

The apparatus used for preparing all arene-tricarbonylchromium complexes was similar to that described by Strohmeier (51). In the photolysis of complexes when light of wavelength greater than 290 nm was desired a 275-watt General Electric sunlamp was used. The light was filtered through cool water and the irradiation of solutions was carried out under nitrogen in a pyrex flask. When either 250 nm or 350 nm light was desired a Rayonet Photochemical Reactor (The Southern New England Ultraviolet Co.) was employed fitted with either RUL 2537 or RUL 3000 lamps having a peak energy output at the indicated wavelengths. Samples were irradiated under argon in a quartz tube fitted with an internal cooling coil.

Elemental microanalyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan. Molecular weight determinations were carried out osmometrically in benzene by Schwarzkopf Microanalytical Laboratory. Infrared spectra were obtained using Beckman IR-18A and IR-4250 spectrophotometers. Varian Associates HA-100 and A-60 spectrometers and a Hitachi Perkin-Elmer R-20B spectrometer were used in obtaining nuclear magnetic resonance spectra. For special cases when only a small amount of sample was available for proton nmr analysis a Bruker HX-90 spectrometer and Nicolet 1089 computer operating in the Fourier Transform mode were employed. Mass spectral analysis was performed on an Associated Electronics Industries MS 902 double focusing spectrometer.

The instrument used for melting points was a Thomas Hoover capillary melting point apparatus. All melting points were uncorrected.

Commercial Compounds

The chemicals obtained from commercial sources are listed in Table VIII.

Prepared Chelating-arene Ligands

Benzobicyclo[2.2.1]heptadiene

Prepared by the procedure of Fieser and Haddadin (52), bp 93-96°, 18-20 mm, lit (53), bp 82.5-83.0°/12 mm; nmr (CCl_4) δ 7.1-6.8 (m, 4), 6.7 (m, 2), 5.8 (m, 2) and 2.2 (m, 2).[1]

Benzobicyclo[2.2.2]octadiene (77)

The method of Kirahonoki and Takano was employed (54). In a stainless autoclave, 25.0 g (312 mmole) of 1,3-cyclohexadiene was heated under nitrogen at 180-190° for 24 hrs. The product was removed from the bomb with several ether rinses

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[1] The compound was prepared by D.K. Wells.

Table VIII. Source of commercial compounds

Compound	Source
Acetone-d_6	Norell Chemical Co., Inc.
Acetonitrile	J.T. Baker Chemical Co. (Baker)
Acroylyl Chloride	Aldrich Chemical Co., Inc., (Aldrich)
Allyl Bromide	Aldrich
Allyl Chloride	Baker
Allyl Lithium	Orgmet Inc.
Allyl Phenyl Ether	Aldrich
Alumina (Woelm neutral)	Waters Associates, Inc.
Ammonium Chloride	Baker
Benzene (thiophene free)	Baker
Benzene-d_6 (C_6D_6)	Norell Chemical Co., Inc.
Benzoyl Peroxide	Baker
Benzyl Alcohol	Baker
Borane (1.0 M in tetrahydrofuran)	Ventron Corporation
Boron Trifluoride Ether	Eastman Organic Chemicals

Table VIII. Continued

Compound	Source
N-Bromosuccinimide	Baker
_n_-Butyl Lithium	Foote Mineral Co.
Calcium Chloride ($CaCl_2$)	Baker
Carbon Monoxide	Matheson Coleman and Bell
Carbon Tetrachloride (CCl_4)	Baker
Chloranil	Eastman Organic Chemicals
Chloroform ($CHCl_3$)	Baker
Chloroform-_d_ ($CDCl_3$)	Baker
1,3-Cyclohexadiene	Aldrich
Diisopropylamine	Aldrich
1,2-Dimethoxyethane (glyme)	Eastman Organic Chemicals
Dimethylsulfoxide-$\underline{d}_6$	Stohler Isotope Chemicals
1,4-Dioxane	Baker
Ethyl Alcohol	Commercial Solvents
Ethyl Ether	Fisher Scientific Co. (Fisher)
Ethyl Vinyl Ether	Baker

Table VIII. Continued.

Compound	Source
Hexacarbonylchromium	Strem Chemicals
Hexane	Baker
Hydrochloric Acid	Fisher
Hydrogen Bromide (48%)	Mallinckrodt
Magnesium Sulfate ($MgSO_4$)	Baker
Mesitylene	Baker
Mercuric Acetate	Baker
Methane Sulfonyl Chloride	Baker
Methanol	Fisher
bis-(Methoxyethyl)Ether	Aldrich
Methyl Iodide	Baker
Molecular Sieves (type 4a)	Baker
Naphthalene	Baker
Nitrogen	Air Products
Paladium on Barium Sulfate (5%)	Strem Chemicals
4-Phenylbutene-1	Chemical Samples Co.

Table VIII. Continued

Compound	Source
5-Phenylpentyne-1	Aldrich
3-Phenylpropanol	Aldrich
3-Phenylpropene	Aldrich
Potassium *t*-Butoxide (resublimed)	Aldrich
Potassium Carbonate	Baker
Potassium Cyanide	Mallinckrodt
Pyridine	Baker
Quinoline (synthetic)	Matheson Coleman and Bell
Silica Gel (60-200 mesh)	Baker
Sodium Bicarbonate	Baker
Sodium Hydroxide	Baker
Sodium Methoxide	Fisher
Sulfuric Acid	Baker
Tetrachloroethane	Mallinckrodt
Tetrahydrofuran (THF)	Baker
Triethylamine	Mallinckrodt
Triphenylphosphine (PPh_3)	Aldrich

and the ethereal solution was suction filtered. The ether was removed by distillation leaving a pale yellow oil which was distilled at reduced pressure to give 4.00 g (20%) of 1,3-cyclohexadiene dimer: bp 60-63°, 3 mm; lit (54), bp 80-83°, 7 mm; nmr (CCl_4) δ 6.50-5.20 (m, 4) and 2.80-0.90 (m, 12). A mixture of 4.0 g (62.4 mmole) of the dimer, 14.8 g of chloranil and 50 ml of xylene was heated to reflux for 20 hr. The work-up of the product mixture and chromatography of the product on 400 g of alumina were carried out exactly as described (53) and gave 1.99 g (51%) of (77); nmr (CCl_4) δ 6.90 (s, 4, ArH), 6.32 (t, J = 5 Hz, 2, -HC=CH-), 4.00-3.61 (m, 2, bridgehead H) and 1.45 (s, 4, $-H_2C-CH_2-$).

5-Phenylpentene-1 (78)

A modification of the Morrison method was employed (55). A mixture of 1.0 g (7.1 mmole) of 5-phenylpentyne-1, 0.020 g of 5% palladium on barium sulfate, 0.040 g of quinoline and 20 ml of ethanol was stirred under hydrogen (729 torr and 303° K) until the uptake of hydrogen reached the calcd 177 ml. The product mixture was filtered and 50 ml of ether was added. The solution was washed successively with two 50-ml portions of water, two 25-ml portions of 10% hydrochloric acid, 25 ml of saturated sodium bicarbonate and 25 ml of water. The ethereal solution was dried ($MgSO_4$), filtered and the ether removed leaving 0.71 g (72%) of the olefin as a colorless oil; nmr (CCl_4) δ 7.08 (s, 5, ArH), 6.15-5.43 (m, 1, $H_2C{=}C\underline{H}-$), 5.17-4.73 (m, 2, $\underline{H}_2C$=CH-) and 2.30-1.10 (m, 6, $-CH_2CH_2CH_2-$). The crude sample (78) was used in the complexation of 78 without further purification.

6-Phenylhexene-1 (79)

The method of Kozacik was followed (56). Treatment of 3-phenylpropanol with 48% hydrogen bromide and sulfuric acid as described by Aspinall (57) gave 3-phenyl-1-bromopropane (84%); nmr (CCl_3) δ 7.17 (s, 5) 3.28 (t, J = 6.1 Hz, 2), 2.90-2.60 (m, 2) and 2.40-1.95 (m, 2). A solution of 15.9 g (84.0 mmole) of 3-phenyl-1-bromopropane in 100 ml of ether was added dropwise to 2.04 g (84.0 mmole) of magnesium and the mixture was stirred at ambient temperature for three hours. The mixture was filtered under nitrogen from unreacted magnesium and the filtrate was heated to reflux. Following dropwise addition of a solution of 10.2 g (84.0 mmole) of allyl bromide in 50 ml of ether the solution was stirred at reflux for eight hours. The cooled product mixture was acidified with 60 ml of 10% hydrochloric acid, the phases separated and the organic layer was washed successively with two 50-ml portions of water, 50 ml of five percent sodium bicarbonate and 100 ml of water. The ethereal solution was dried ($MgSO_4$), filtered and the ether was removed (vacuum rotary evaporation) and gave 10.6 g (56%) of crude 6-phenylhexene-1: nmr (CCl_4) δ 7.18 (s, ~5, ArH), 6.10-5.35 (m, ~1, $-\underline{H}C$=CH_2), 5.11-4.70 (m, ~2, -HC=$C\underline{H}_2$) and 2.80-1.30 (m, ~8,

$-CH_2-$). The material was used in complexation of 79 without further purification.

1,4-Dihydronaphthalene (80)

The compound was prepared according to the method of Hückel (58) 0.156 mole scale. Work-up yielded 19 g of a white solid; mp; 45-55°; lit (58) mp 55° for a 60:40 mixture of 1,4-dihydronaphthalene:naphthalene (56% absolute yield of 1,4-dihydronaphthalene). The mixture was used in the complexation of 80 without separation from naphthalene.

Allyl 3-tolyl ether

A mixture of 3.50 g (32.4 mmole) of 3-methylphenol, 2.0 g of sodium methoxide, 25 ml of methanol and 5.0 ml allyl chloride was heated to reflux for 4.0 hr. Ether (100 ml) was added to the cooled product mixture and the solution was washed successively with 50 ml of water, 50 ml of five percent sulfuric acid, 50 ml of five percent sodium hydroxide and 50 ml of water. The ethereal solution was dried ($CaCl_2$) and the solvent removed giving 3.19 g of allyl 3-tolyl ether as a colorless oil (66%); nmr (CCl_4) δ 7.10-6.32 (m, 4, ArH), 6.20-5.60 (m, 1, $-C\underline{H}=CH_2$), 5.45-4.85 (m, 2, $-CH=C\underline{H}_2$) 4.44-4.17 (m, 2, $-CH_2-$) and 2.67 (s, 3, $-CH_3$).

Allyl 3,5-xylyl ether

A mixture of 3.50 g (28.7 mmole) of 3,5-dimethylphenol, 2.0 g of sodium methoxide, 25 ml of methanol and five ml of allyl chloride was heated to reflux for 4.0 hr. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether. The ethereal solution was washed successively with 50 ml of water, 50 ml of five percent sulfuric acid, 50 ml of five percent sodium hydroxide and 50 ml of water. The solution was dried ($CaCl_2$), filtered and the ether was removed (vacuum rotary evaporation) and gave 3.96 g allyl 3,5-xylyl ether (85%); nmr (CCl_4) δ 6.36 (s, 3, ArH), 6.12-5.72 (m, 1, $-C\underline{H}=CH_2$), 5.40-5.01 (m, 2, $-CH-C\underline{H}_2$) 4.43-4.28 (m, 2, $-CH_2-$) and 2.21 (s, 6, $-CH_3$).

Benzyl vinyl ether

A modification of the Watanabe method (59) was used. A mixture of 27.0 g (250 mmole) of benzyl alcohol, 54.0 g of ethyl vinyl ether and 1.5 g of mercuric acetate was heated to reflux for six hr. The product mixture was treated with anhydrous potassium carbonate and the low boiling components were removed (vacuum rotary evaporation). Distillation at lower pressure yielded 4.75 g (14.2%) of benzyl vinyl ether: bp 73-74°, 10.0 mm; Lit (59) 103-104°, 25 mm; nmr (CCl_4) δ 7.23 (s, 5, ArH), 6.62-6.25 (four line X portion of ABX, 1, $-\underline{H}C=CH_2$), 4.68 (s, 2, $PhCH_2-$) and 4.32-3.88 (eight line AB portion of ABX, 2, $-HC=C\underline{H}_2$).

γ-Phenylbutyronitrile (81)

A modification of Braun's method (60) was used. A solution of 33.0 g (243 mmole) of 3-phenylpropanol in 200 ml of pyridine was cooled to -10° and with stirring 37.0 g (323 mmole) of methanesulfonyl chloride was added dropwise over a period of 45 min. The mixture was allowed to stand for one hr when 100 ml of ether and 100 ml of cold 3.0 M hydrochloric acid were added. The phases were separated and the ethereal solution was washed successively with five 50-ml portions of 3.0 M hydrochloric acid, 50 ml of water, 50 ml of saturated sodium bicarbonate and 50 ml of water. The ethereal solution was dried ($MgSO_4$) and filtered. Removal of the ether by distillation provided the 3-phenyl-*n*-propyl methanesulfonate. The sulfonate was dissolved in 150 ml of acetonitrile. A solution of potassium cyanide (27.0 g) in 65 ml of water was added and the mixture was heated to reflux overnight. The product mixture was transferred to a separatory funnel and 100 ml of ether was added. The water soluble components were removed with several water washes. The ethereal solution was dried ($MgSO_4$), filtered and the ether was removed by distillation. The remaining product was purified by distillation at reduced pressure and provided 23.8 g (68%) of **81**: bp 137-139°, 16 mm; lit (60) 142-145°, 16 mm; nmr (CCl_4) δ 7.12 (s, 5), 2.70 (t, $J = 6.0$ Hz, 4) and 2.32-1.67 (m, 4).

β-Phenylpropionitrile

The above procedure was followed, 0.37 mole scale using 2-phenylethanol, and provided the nitrile: bp 111-112°, 5 mm; lit (61) 114-118°, 6 mm.[1]

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[1] The compound was prepared by D. Powers.

1,3-Diallyloxybenzene (82)

A mixture of 4.00 g (36.4 mmole) of resorcinol, 4.0 g of sodium methoxide, 7.2 ml of allyl chloride and 25.0 ml of methanol was heated to reflux for 4.0 hr. The cooled product mixture was poured into 200 ml of water and the mixture was extracted with two 50-ml portions of ether. The combined ether extract was washed with 100-ml portions of five percent sodium hydroxide, five percent sulfuric acid and water. The ethereal solution was dried ($MgSO_4$), filtered and the ether was removed by distillation through a small column and left 1.80 g of crude 82 (26%) as a pale yellow oil. The material was purified by thick layer chromatography (90:10, v/v, hexane: ether eluant) and produced colorless 1,3-diallyloxybenzene, 0.75 g; nmr (CCl_4) δ 7.18-6.70 (m, 1, ArH), 6.50-6.15 (m, 3, ArH), 6.15-5.60 (m, 6, $-CH=CH_2$) and 4.55-4.28 (m, 4, $-CH_2-$).

α,α',α''-Tribromomesitylene

A solution of 3.00 g (25.0 mmole) of mesitylene, 13.5 g (75.8 mmole) of N-bromosuccinimide, 0.030 g of benzoyl peroxide and 250 ml of carbon tetrachloride was stirred and heated to reflux overnight. The cooled product mixture was filtered and the filtrate was washed successively with 100 ml of water, two 50-ml portions of 1.0 M sodium hydroxide and 50 ml of water. The organic phase was dried ($CaCl_2$), filtered and the solvent was removed (vacuum rotary evaporation) and yielded 6.50 g (73%) of the tribromide; mp 95.5-96.5°; lit (62) 93°;

nmr (CCl_4) δ 7.28 (s, 3) and 6.38 (s, 6).

Prepared Tricarbonylchromium Complexes

(Triacetonitrile)tricarbonylchromium

The material was prepared according to the procedure of King (5) which was modified by Wells (63).

syn-(Benzobicyclo[2.2.1]heptadiene)tricarbonylchromium (26)

A mixture of 2.0 ml of benzobicyclo[2.2.1]heptadiene, (triacetonitrile)tricarbonylchromium (prepared from 1.5 g of hexacarbonylchromium) and 20 ml of dioxane was heated to reflux under a nitrogen atmosphere in a Strohmeier apparatus for 5 min. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether and the solution was washed with five 200-ml portions of water. The organic phase was dried ($MgSO_2$), filtered and the solvent was removed. The residue was chromatographed on 130 g of silica gel (1:1, v/v, benzene-hexane eluant) and the single yellow band was collected yielding a yellow solid upon removal of the solvent. The product was taken up in 20 ml of chloroform and crystals developed when an equal volume of pentane was added. Refrigeration gave 0.67 g of the complex (35% based on hexacarbonylchromium): mp (decompn) 138°, lit (63) 132°; ir (ether), 1891 (vs) cm^{-1}; ir (hexane), 1973 (vs) and 1904 (vs) cm^{-1}; nmr (C_6D_6) δ 6.50 (m, 2, -HC=CH-), 4.61 (AA'BB' pattern, ν_a ~5.00,

ν_b ~4.21, 4), 2.90 (m, 2, bridgehead H) and 1.90-1.47 (m, 2, $-CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 279 (8), 278 (21) parent ion, 250 (2), 222 (10) and 194 (100).

Anal. Calcd for $C_{14}H_{10}CrO_3$: C, 60.44; H, 3.63. Found: C, 60.46; H, 3.71.

syn-(Benzobicyclo[2.2.2]octadiene)tricarbonylchromium (29)

A solution of 1.00 g (6.41 mmole) of benzobicyclo-[2.2.2]octadiene in 20 ml of dioxane was added to (triacetonitrile)tricarbonylchromium (prepared from 1.5 g of hexacarbonylchromium) and the mixture was heated to reflux for 10 min. The product mixture was rinsed into a separatory funnel with 150 ml of ether and washed with five 200-ml portions of water, dried ($MgSO_4$), filtered and the ether was removed. The resulting yellow oil was chromatographed on 130 g of silica gel (80:20, v/v, pentane:ether eluant) and the long yellow band was collected and gave 0.590 g of the complex (31.5%) based on benzobicyclo[2.2.2]octadiene: mp (decompn) 150.5°; ir (ether) 1890 (vs) cm^{-1}; nmr ($CDCl_3$) δ 6.45 (t, J = 5 Hz, 2, -HC=CH-), 5.30 (AA'BB' pattern, ν_a ~5.53, ν_b ~5.06, 4), 3.60 (m, 2, bridgehead H), and 1.70-1.30 (m, 4, $-H_2C-CH_2-$); nmr (C_6D_6) δ 6.11 (t, J = 5 Hz, 2, -HC=CH-), 4.51 (AA'BB' pattern, ν_a ~4.74, ν_b ~4.28, 4), 2.90 (m, 2, bridgehead H), 0.99 (m, 2, exo -CH-CH-) and 0.87 (m, 2, endo -CH-CH-)[1]; mass spectrum

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[1] The solvent effect was identical to that observed for the syn isomer 26; see reference 63.

(70 eV) m/e (rel. intensity) 293 (5.83), 292 (18.3), parent ion, 236 (9.17), 208 (100), 182 (18.8), 130 (22.1) and 52 (39.1). Exact mass. Calcd for $C_{15}H_{12}CrO_3$, 292.0192; found, 292.0181 ± .002. Anal. Calcd for $C_{15}H_{12}CrO_3$: C, 61.64; H, 4.15. Found: C, 61.46; H, 4.18.

syn-(Dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (27)

The method of King (5) was used as modified by Trahanovsky and Baumann (64).[1]

(3-Phenylpropene)tricarbonylchromium (31)

A mixture of two ml of allylbenzene (15.1 mmole), 1.50 g (6.81 mmole) of hexacarbonylchromium and 25 ml of glyme was refluxed for 14 hrs at which time five ml of diglyme was added. The mixture was refluxed for an additional 34 hrs and the cooled product mixture was rinsed into a separatory funnel with 50 ml of ether. The ethereal solution was washed successively with five 200-ml portions of water, dried ($MgSO_4$), filtered and the solvent removed yielding a yellow residue. Chromatography of the mixture on 120 g of silica gel (hexane eluant) furnished a single band which gave 0.41 g (1.61 mmole, 23.6%) of (3-phenylpropene)tricarbonylchromium as an oil: ir (ether) 1965 (w) 1892 (vs) cm^{-1}; nmr (CCl_4) δ 5.2-6.0 (m, 3, $HC{=}CH_2$), 5.1 (m, 5, ArH), and 3.1 (m, 2, $ArCH_2$); mass spectrum (70 eV)

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[1] The complex was prepared by C. Baumann.

m/e (rel. intensity) 255 (1.25), 254 (29.0) parent ion, 226 (0.50), 198 (10.1), 170 (100), 118 (40.0) and 91 (25.5). *Exact mass*. Calcd for $C_{12}H_{10}CrO_3$, 254.0035; found, 254.0050 ± .003.

(4-Phenylbutene-1)tricarbonylchromium (32)

A mixture of 4.0 ml of 4-phenylbutene-1, 3.00 g (13.6 mmole) of hexacarbonylchromium, 25 ml of glyme and five ml of diglyme was heated to reflux for 46 hr in a Strohmeier apparatus. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether and washed with five 200-ml portions of water, dried ($MgSO_4$), filtered and the volume of the solution was reduced to about 10 ml. Chromatography on 130 g of silica gel (80:20, v/v, hexane:ether) produced a single band which gave 2.78 g (10.4 mmole, 76%) of the complex (32) as a yellow oil: ir (ether) 1969 (s) and 1901 (vs) cm^{-1}; ir (pentane) 1988 (vs) and 1918 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.10-5.32 (m, 6, ArH and $H_2C{=}C\underline{H}$-), 5.03 (d, $J = 17$ Hz, 1, *trans*-$HH̲C{=}CH$-), 4.99 (d, $J = 10$ Hz, 1, *cis*-$\underline{H}HC{=}CH$-) and 2.80-2.18 (m, 4, $-CH_2CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 269 (5.20), 268 (16.9) parent ion, 240 (0.65), 212 (2.60), 184 (85.8) and 91 (100). *Exact mass*. Calcd for $C_{13}H_{12}CrO_3$, 268.0192; found, 268.0189 ± .002.

(5-Phenylpentene-1)tricarbonylchromium (33)

A mixture of 0.690 g (4.73 mmole) of 5-phenylpentene-1, 1.5 g of hexacarbonylchromium, 25 ml of glyme and 10 ml of diglyme was heated to reflux in a Strohmeier apparatus overnight. The product mixture was rinsed into a separatory funnel with 50 ml of ether and washed with five 200-ml portions of water, dried ($MgSO_4$) filtered and the volume of the solution was reduced to about 10 ml. Chromatography on 130 g of silica gel (90:10, v/v, hexane:ether) gave a single band which produced 0.430 g (1.52 mmole, 32%) of complex 33 as a yellow oil: ir (ether) 1970 (s) and 1902 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.20-5.28 (m, 6, ArH and $H_2C{=}C\underline{H}$-), 5.02 (d, J = 17.0 Hz, 1, trans-$H\underline{H}C{=}CH$-), 4.94 (d, J = 10.0 Hz, 1, cis-$H\underline{H}C{=}CH$-) and 2.70-1.20 (m, 6, -$CH_2CH_2CH_2$-); mass spectrum (70 eV) m/e (rel. intensity) 283 (6.04), 282 (20.0) parent ion, 254 (0.377), 226 (0.566), 198 (68.0), 146 (21.1) and 91 (100). Exact mass. Calcd for $C_{14}H_{14}CrO_3$, 282.0348; found, 282.0347 ± .002.

(6-Phenylhexene-1)tricarbonylchromium (34)

A mixture of 1.50 g (9.37 mmole) of crude 6-phenylhexene-1, 2.0 g of hexacarbonylchromium, 20 ml of glyme and 15 ml of diglyme was heated to reflux in a Strohmeier apparatus for 20 hr. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether and the water soluble components were removed with five 200-ml water washes. The organic layer was dried ($MgSO_4$), filtered and the volume of solution was reduced to about five ml. Chromatography of the material on 140 g of silica gel (80:20, v/v, hexene:ether) gave 0.640 g (2.16 mmole, 23%) of 34 as a yellow oil: ir (ether) 1965 (w) and 1900 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.22-5.25 (m, 6, ArH and -$\underline{H}C{=}CH_2$), 5.20-4.75 (m, 2, -$HC{=}C\underline{H}_2$) and 2.60-1.20 (m, 8, -CH_2-); mass spectrum (70 eV) m/e (rel. intensity) 297 (1.56), 296 (4.55) parent ion, 212 (6.14), 160 (15.6), 91 (100) and 52 (27.3). Exact mass. Calcd for $C_{15}H_{16}CrO_3$, 296.0505; found, 296.0498 ± .0015.

(1,4-Dihydronaphthalene)tricarbonylchromium (30)

A solution of 3.0 g of the 1,4-dihydronaphthalene - naphthalene mixture (obtained from the experiment described on page 81), (triacetonitrile)tricarbonylchromium (prepared from 1.50 g of hexacarbonylchromium), and 20 ml of dioxane was heated to reflux for 45 min at which time the solution was cooled and 100 ml of ether was added. The ethereal solution was washed with five 200-ml portions of H_2O, dried ($MgSO_4$), filtered and the ether was removed. The residue was chromatographed on 130 g of silica gel (1:1, v/v, benzene-hexane eluant) and the yellow band was collected to yield (1,4-dihydronaphthalene)tricarbonylchromium, 0.360 g (1.35 mmole, 20%): mp 113 - 115°; ir (ether), 1898 (vs) cm^{-1}; nmr (C_6D_6) δ 5.50 - 5.20 (s, 2, -$HC{=}CH$-), 4.49 (s, 4, ArH) and 2.62 (s, 4, -CH_2-); mass spectrum (70 eV) m/e (rel. intensity), 267 (8.17), 266 (30.2) parent ion, 210 (16.8), 182 (16.0) and 52 (100). Anal. Calcd for $C_{13}H_{10}CrO_3$: C, 58.65; H, 3.79. Found: C, 58.78; H, 3.77.

(Allyl phenyl ether)tricarbonylchromium (39)

A mixture of 1.00 g (7.46 mmole) of allyl phenyl ether, 1.5 g of hexacarbonylchromium and 50 ml of glyme was heated to reflux overnight in a Strohmeier apparatus. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether and the ethereal solution was washed with five 200-ml portions of water, dried ($MgSO_4$), filtered and the solution volume was reduced to about five ml. Chromatography of the yellow material on 120 g of silica gel (80:20, v/v, hexane: ether) gave 0.680 g (2.52 mmole, 34%) of 39: mp 43.5-45°; ir (ether) 1967 (s) and 1900 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.16-4.98 (m, 8, ArH and $-HC{=}CH_2$) and 4.53-4.38 (m, 2, $-C\underline{H}_2CH{=}CH_2$); mass spectrum (70 eV) m/e (rel. intensity) 271 (12.0), 270 (41.4) parent ion, 214 (7.68), 186 (94.9), 145 (100), 94 (27.6) and 52 (53.3). Exact mass. Calcd for $C_{12}H_{10}CrO_4$, 269.9984; found, 269.9986 ± .002. Anal. Calcd for $C_{12}H_{10}CrO_4$; C, 53.33; H, 3.74. Found: C, 53.28; H, 3.66.

(Allyl 3-tolyl ether)tricarbonylchromium (40)

A mixture of 1.00 g (6.75 mmole) of allyl 3-tolyl ether, 1.5 g hexacarbonylchromium, 30 ml of glyme and five ml of diglyme was heated to reflux in a Strohmeier apparatus for 24 hr. The cooled product mixture was rinsed into a separatory funnel with 100 ml of ether and the solution was washed with five 100-ml portions of water. The ethereal solution was dried (MgSO$_4$), filtered and the solvent was removed by rotary evaporation at reduced pressure. Chromatography of the residue on 130 g of silica gel (80:20, v/v, hexane:ether) produced a single yellow band. Isolation gave 0.488 g (1.72 mmole, 25.4%) of the complex (**40**): mp 39.5-40.5°; ir (ether) 1962 (s) and 1894 (vs) cm^{-1}; nmr (C$_6$D$_6$) δ 5.88-5.46 (m, 1, -C$\underline{\text{H}}$=CH$_2$), 5.24-4.90 (m, 2, -CH=C$\underline{\text{H}_2}$), 4.77 (t, J = 6.2 Hz, 1, *m*-ArH), 4.48 (s, 1, *o*-ArH), 4.33 (d, J = 6.2 Hz, 1, *o*-ArH), 3.96 (d, J = 6.2 Hz, 1, *p*-ArH), 3.86-3.70 (m, 2, -CH$_2$-) and 1.69 s, 3, -CH$_3$); mass spectrum (70 eV) m/e (rel. intensity) 285 (10.5), 284 (34.4) parent ion, 256 (37.5), 199 (100) and 159 (25.0). *Exact mass*. Calcd for C$_{13}$H$_{12}$CrO$_4$, 284.0141; found, 284.0136 ± 0.0014.

(Allyl 3,5-xylyl ether)tricarbonylchromium (**41**)

A mixture of 2.0 g (12.3 mmole) of allyl 3,5-xylyl ether, 2.0 g of hexacarbonylchromium, 30 ml of glyme and 10 ml of diglyme was heated to reflux in a Strohmeier apparatus for 36 hr. The cooled product mixture was rinsed into a separatory funnel with 75 ml of ether. The ethereal solution was washed with five 100-ml portions of water, dried (MgSO$_4$), filtered and the ether was removed by rotary evaporation at reduced pressure. The residue was chromatographed on 130 g of silica gel and produced a single yellow band. Isolation gave 0.827 g (2.78 mmole, 30.4%) of 41: mp 66.0-68.5°; ir (ether) 1955 (s) and 1889 (vs) cm^{-1}; nmr (C_6D_6) δ 5.92-5.52 (m, 1, -C$\underline{H}$=CH$_2$), 5.24-4.94 (m, 2, -CH=C$\underline{H}_2$), 4.43 (s, 2, *o*-ArH), 3.94 (s, 1, *p*-ArH), 3.90-3.79 (m, 2, -CH$_2$-), and 1.76 (s, 6, -CH$_3$); mass spectrum (70 eV) m/e (rel. intensity) 299 (10.5), 298 (25.4) parent ion, 242 (5.26), 214 (100), 173 (73.6) and 122 (5.15). Exact mass. Calcd for $C_{14}H_{14}CrO_4$, 298.0297; found, 298.0302 ± 0.0015.

(Benzyl vinyl ether)tricarbonylchromium (38)

A mixture of 1.50 g (11.2 mmole) of benzyl vinyl ether, 2.0 g of hexacarbonylchromium, 30 ml of glyme and five ml of diglyme was heated to reflux in a Strohmeier apparatus for 40 hr. The work-up and chromatography used in the isolation of (allyl phenyl ether)tricarbonylchromium (39) was carried out and gave a yellow oil. Crystallization of the material from pentane gave 0.490 g (1.81 mmole, 16%) of 38: mp 49.5-50.0°; ir (ether) 1968 (m) and 1902 (vs) cm^{-1}; nmr (acetone-*d*$_6$) δ 6.70-6.46 (four line X portion of ABX, 1, -$\underline{H}$C=CH$_2$), 5.76-5.40 (m, 5, ArH), 4.58 (s, 2, ArCH$_2$-) and 4.46-4.05 (eight line AB portion of ABX, 2, -HC=C$\underline{H}_2$); mass spectrum (70 eV) m/e (rel. intensity) 271 (1.32), 270 (4.22) parent ion, 214 (1.32), 186 (7.57), 182 (15.0) and 91 (100). Exact mass. Calcd for $C_{12}H_{10}CrO_4$, 269.9984; found, 269.9982 ± .0014. Anal. Calcd for $C_{12}H_{10}CrO_4$; C, 53.33; H, 3.74. Found: C, 53.41; H, 3.95.

(Benzylalcohol)tricarbonylchromium

Prepared according to procedure of Nicholls and Whiting (4) as modified by Wells (63).[1]

(Benzyl acrylate)tricarbonylchromium (42)

A volume of 0.21 ml (0.23 g, 2.6 mmole) of acrylyl chloride was added at ambient temperature to a stirred solution of 0.79 g (2.6 mmole) of pyridine, 0.5 g (2.1 mmole) of (benzyl alcohol)tricarbonylchromium and 20 ml of ether. The solution was stirred for one hr under nitrogen. The product mixture was filtered and the filtrate was subjected to vacuum rotary evaporation leaving 0.15 g (0.50 mmole, 24%) of 42 as a yellow oil: ir (ether) 1968 (s), 1903 (vs) and 1740 (s) cm^{-1}; nmr (acetone-d_6) δ 6.48-5.40 (m, 8, ArH and $-HC{=}CH_2$) and 4.99 (s, 2, $ArCH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 299 (6.38), 298 (19.1) parent ion, 270 (0.91), 242 (5.45), 227 (5.45), 214 (57.2), 91 (27.3) and 52 (100). Exact mass. Calcd for $C_{13}H_{10}CrO_5$, 297.9933; found, 297.9935 ± .0015.

(1,3-Diallyloxybenzene)tricarbonylchromium (54)

In a Strohmeier apparatus a mixture of 0.620 g (3.26 mmole) of 1,3-diallyloxybenzene, 1.0 g of hexacarbonylchromium, 20 ml of glyme and 15 ml of diglyme was heated to reflux for 48 hr. The product mixture was rinsed into a separatory

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[1] The complex was prepared by D.K. Wells.

funnel with 100 ml of ether where the water soluble components were removed with several 100-ml water washes. The ethereal solution was dried ($MgSO_4$), filtered and the ether was removed (rotary evaporation) and gave 0.393 g (1.21 mmole, 37%) of **54**: ir (ether) 1935 (s) and 1898 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.70-4.90 (m, 9, ArH_3 and $-CH=CH_2$) and 4.75-4.35 (m, 4, $-CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 327 (10.2), 326 (37.3) parent ion, 242 (72.0), 108 (100), 220 (51.7) and 201 (67.8). *Exact mass*. Calcd for $C_{15}H_{14}CrO_5$, 326.0246; found, 326.0262 ± .0016.

(1,3,5-Trihomoallylbenzene)tricarbonylchromium (**55**)

A solution of 2.00 g (5.60 mmole) of α,α',α''-tribromomesitylene in 50 ml of ether was cooled to -77° with stirring and under nitrogen. Allyl lithium (17.0 mmole, 20 ml 0.85 $\underline{M}$ in ether) was added slowly and the mixture was stirred for 30 min. The solution was allowed to warm to ambient temperature and after 10 ml of water was added the solution was transferred to a separatory funnel. The phases were separated and the ethereal solution was washed with two 50-ml portions of water, dried ($MgSO_4$), filtered and the ether was removed by rotary evaporation at reduced pressure. The colorless oil which remained was quickly dissolved in 10 ml of glyme and 10 ml of diglyme.[1] The solution was transferred to a Stroh-

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[1] The material was suspected to have undergone polymerization in a previous experiment.

meier apparatus along with 1.0 g of hexacarbonylchromium where it was heated to reflux for 24 hr. The cooled product mixture was rinsed into a separatory funnel with 75 ml of ether and the water soluble components were removed with several 100-ml water washes. The ethereal solution was dried ($MgSO_4$), filtered and the solvent removed (vacuum rotary evaporation). The residue was chromatographed on 40 g of silica gel (50:50, v/v, hexane-ether eluant) and the yellow band produced 0.486 g (1.29 mmole, 17%) of 55 as a yellow oil: ir (ether) 1960 (w), 1895 (vs) cm^{-1}; nmr (C_6D_6) δ 5.95-5.30 (m, 3, $-C\underline{H}=CH_2$), 5.20-4.15 (m, 9, ArH_3 and $-CH=C\underline{H_2}$) and 2.90-1.70 (m, 12, $-CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 377 (3.64), 376 (9.77) parent ion, 292 (100), 251 (54.6), 206 (97.3), 199 (60.9) and 130 (100). Exact mass. Calcd for $C_{21}H_{24}CrO_3$, 376.1131; found, 376.1121 ± .0019.

(Phenylacetonitrile)tricarbonylchromium

A mixture of 1.5 ml of phenylacetonitrile, 1.00 g (4.55 mmole) of hexacarbonylchromium, 30 ml of glyme and five ml of diglyme was heated to reflux in a Strohmeier apparatus for 22 hr. The product mixture was rinsed into a separatory funnel with 100 ml of ether and the ethereal solution was washed with five 200-ml portions of water, dried ($MgSO_4$), filtered and the ether was removed on the rotary evaporator giving a yellow oil. Chromatography of the residue on 130 g of silica gel (60:40, v/v, hexane:ether eluant) gave two yellow bands. The second band produced 0.183 g (0.72 mmole, 16%) of crystalline (phenylacetonitrile)tricarbonylchromium: mp 66.0-68.5°; nmr ($CDCl_3$) δ 5.32 (s, 5, ArH) and 3.54 (s, 2, $-CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 254 (15.9), 253 (63.6), 197 (4.55), 169 (100), 117 (36.4) and 52 (61.4). Exact mass. Calcd for $C_{11}H_7CrNO_3$, 252.9831; found, 252.9833 ± .0013.

(2-Phenylethylamine)tricarbonylchromium (51)

The reduction procedure of Brown was followed (65). (Phenylacetonitrile)tricarbonylchromium (0.183 g, 0.720 mmole) was dissolved in four ml of tetrahydrofuran and 2.1 mmole of borane was added (2.1 ml, 1.0 M borane in tetrahydrofuran). The mixture was stirred under nitrogen at ambient temperature for 4.0 hr when two ml of ethanol was slowly added followed by the addition of 100 ml of ether. The ethereal solution was washed with three 50-ml portions of water. The ether phase was acidified with dilute hydrochloric acid and extracted with two 50-ml portions of water. The two aqueous extracts were combined and neutralized with 10% sodium hydroxide and extracted with two 50-ml portions of ether. The combined ether extract was dried ($MgSO_4$), filtered and the ether removed to yield 0.025 g (0.10 mmole, 13%) of 51 as an oil: ir (ether) 1966 (s) and 1897 (vs) cm^{-1}; mass spectrum (70 eV) m/e (rel. intensity) 258 (3.09), 257 (10.4) parent ion, 229 (15.1), 201 (10.9), 173 (100) and 121 (21.8). Exact mass. Calcd for

$C_{11}H_{11}CrNO_3$, 257.0144; found, 257.0140 ± .0013.

(3-Phenylpropylamine)tricarbonylchromium (49)

A mixture of 2.00 g (15.3 mmole) of β-phenylpropionitrile, 1.00 g (4.55 mmole) of hexacarbonylchromium, 20 ml of glyme and 10 ml of diglyme was heated to reflux in a Strohmeier apparatus for 60 hr. The cooled mixture was transferred to a separatory funnel with 100 ml of ether and the solution was washed with five 200-ml portions of water, dried ($MgSO_4$), filtered and the ether was removed (vacuum rotary evaporation). The residue was chromatographed on 130 g of silica gel (60:40, v/v, hexane:ether eluant). The single yellow band produced a yellow solid which was recrystallized from ether-pentane and yielded 0.629 g of (β-phenylpropionitrile)tricarbonylchromium (52%): mp 73-75°. The nitrile complex was reduced following the procedure of Brown (65) where 0.629 g (2.36 mmole) was taken up in five ml of tetrahydrofuran and 3.0 mmole of borane was added (3.0 ml of 1.0 M borane in tetrahydrofuran). The mixture was stirred under nitrogen for 4.0 hr. Work-up of the solution as described in the preparation of (2-phenylethylamine)tricarbonylchromium (51) yielded 0.231 g (0.85 mmole, 36%) of 49 as an oil: ir (ether) 1968 (s) and 1898 (vs) cm^{-1}; nmr (acetone-d_6) δ 5.80-5.25 (m, 5, ArH), 3.23 (t, J = 6.5 Hz, 2, $-C\underline{H}_2NH_2$), 2.70-2.25 (m, 2, $ArCH_2-$) and 2.57-1.70 (m, 4, $-C\underline{H}_2CH_2N\underline{H}_2$); mass spectrum (70 eV) m/e (rel. intensity) 272 (1.67), 271

(6.25) parent ion, 243 (8.75), 215 (1.67), 187 (100), 159 (50.0), 135 (7.5) and 91 (20.8). Exact mass. Calcd for $C_{12}H_{13}CrNO_3$, 271.0301; found, 271.0297 ± .0014.

(4-Phenylbutylamine)tricarbonylchromium (53)

A mixture of 0.75 g (5.17 mmole) of γ-phenylbutyronitrile, 1.00 g of hexacarbonylchromium and 20 ml of glyme was heated to reflux in a Strohmeier apparatus for 44 hr. The cooled product mixture was rinsed into a separatory funnel where the water soluble components were removed with several 200-ml water washes. The ethereal solution was dried ($MgSO_4$), filtered and ether was removed by rotary evaporation at reduced pressure. Chromatography of the residue on 120 g of silica gel (80:20, ν/ν, hexane:ether) furnished a yellow residue which was recrystallized from ether-pentane to give 0.330 g of (γ-phenylbutyronitrile)tricarbonylchromium (26%): mp 67.5-71°. A solution of 0.330 g (1.17 mmole) of the complex in four ml of tetrahydrofuran was reduced according to the procedure of Brown (65). The solution was stirred under nitrogen while 2.5 mmole of borane was added (2.5 ml of 1.0 M borane in tetrahydrofuran). The mixture was allowed to react for five hrs. Work-up as described in the preparation of (2-phenylethylamine)tricarbonylchromium (51) gave 0.115 g (0.40 mmole, 34%) of 53 as a yellow oil: ir (ether) 1965 (s) and 1895 (vs) cm^{-1}; nmr (acetone-d_6) δ 5.80-5.25 (m, 5, ArH), 3.40-2.95 (m, 2, $-C\underline{H}_2NH_2$), 2.80-2.18 (m, 2, $ArCH_2-$) and 1.95-1.40 (m, 6, $-C\underline{H}_2C\underline{H}_2CH_2N\underline{H}_2$); mass spectrum (70 eV) m/e (rel. intensity) 286 (0.593), 285 (1.61) parent ion, 229 (2.39), 201 (2.94), 149 (100) and 91 (41.7). *Exact mass.* Calcd for $C_{13}H_{15}CrNO_3$, 285.0457; found, 285.0467 ± .0014.

Prepared Arene-chelate Complexes

(η^8-Benzobicyclo[2.2.1]heptadiene)dicarbonylchromium (**25**)

A solution of 0.100 g (0.36 mmole) of *syn*-(benzobicyclo[2.2.1]heptadiene)tricarbonylchromium (**26**) in 100 ml of ether was irradiated with light of wavelength >290 nm for 65 min. During the reaction the color of the solution changed from straw to orange-red and the reaction progress was followed by observation of changes in the ir spectrum of the solution with time. The ether was removed (vacuum rotary evaporation) and the orange residue was taken up in 10 ml of hexane and decanted from some decomposition product. The volume of the hexane solution was reduced to about five ml and cooling gave 0.0420 g (0.168 mmole, 46.6%) of **25**: mp (decompn) 73°; ir (ether) 1937 (vs) and 1878 (vs) cm^{-1}; ir (hexane), 1939 (vs) and 1877 (vs) cm^{-1}; nmr (C_6D_6) δ 4.90 (AA'BB' pattern, ν_a ~5.38, ν_b ~4.43, 4), 2.70 (m, 2, -HC=CH-), 2.55 (m, 2, bridgehead H) and 1.20-0.60 (m, 2, $-CH_2-$); mass spectrum (70 eV) m/e (rel. intensity) 251 (12), 250 (43) parent ion, 222 (4), 194 (52) and 52 (100). *Exact mass.* Calcd for $C_{13}H_{10}CrO_2$, 250.0086;

found, 250.0081 ± .0013. Anal. Calcd for $C_{13}H_{10}CrO_2$: C, 62.40; H, 4.04. Found: C, 62.15; H, 3.99. Molecular weight: Calcd, 250; found, 254.

(η^8-Dibenzobicyclo[2.2.2]octatriene)dicarbonylchromium (28)

A solution of 0.0500 g of syn-(dibenzobicyclo[2.2.2]octatriene)tricarbonylchromium (27) in 50 ml of ether was irradiated for 45 min with light of wavelength >290 nm. The color change was from straw to orange. The product mixture was subjected to vacuum rotary evaporation and the volume of ether was reduced to about five ml. An equal volume of pentane was added and the mixture was refrigerated yielding 0.0253 g (0.08 mmole, 55%) of red 28: mp (decompn) 67°; ir (ether) 1923 (vs) and 1872 (vs) cm^{-1}; nmr (C_6D_6) δ 7.30-6.70 (m, 4, ArH), 4.50 (AA'BB' pattern ν_a ~4.98, ν_b ~4.02, 4), 3.80 (m, 2, bridgehead H) and 2.75 (m, 2, -HC=CH-); mass spectrum (22 eV) m/e (rel. intensity) 312 (4.0) parent ion, 284 (4.0), 256 (6.0) and 204 (100). Exact mass. Calcd for $C_{18}H_{12}CrO_2$, 312.0242; found, 312.0250 ± .003.

(η^8-4-Phenylbutene-1)dicarbonylchromium (35)

A solution of 0.100 g (0.373 mmole) of (4-phenylbutene-1)-tricarbonylchromium (32) in 100 ml of ether in a Pyrex flask was irradiated with light of wavelength > 290 nm for 45 min. The color of the solution changed from straw to red-orange. The ether was removed from the product mixture and the residue was dissolved in five ml of pentane. Cooling gave 0.047 g (0.196 mmole, 52.5%) of 35: mp 74-75°, ir (ether) 1925 (vs) and 1971 (vs) cm^{-1}; ir (pentane) 1939 (vs) and 1889 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 5.84-5.55 (m, 3, ArH), 5.09 (d, J = 6.0 Hz, 1, *o*-ArH), 4.64 (t, J = 6.0 Hz, 1, *m*-ArH) 3.74-3.44 (m, 1, $H_2C{=}C\underline{H}$-), 3.02-2.60 (m, 2, $-C\underline{H}_2CH{=}CH_2$), 2.81 (d, J = 13.0 Hz, 1, *trans*-$H\underline{H}C{=}CH$-), 2.47-2.23 (m, 1, $ArC\underline{H}HCH_2$-), 1.91-1.56 (m, 1, $ArCH\underline{H}CH_2$-), and 1.62 (d, J = 8.1 Hz, 1, *cis*-$H\underline{H}C{=}CH$-); mass spectrum (70 eV) m/e (rel. intensity) 241 (9.51), 240 (34.3) parent ion, 212 (2.38), 184 (100), 91 (22.9). *Exact mass*. Calcd for $C_{12}H_{12}CrO_2$, 240.0242; found, 240.0248 ± .002. *Anal*. Calcd for $C_{12}H_{12}CrO_2$: C, 59.99; H, 5.04. Found: C, 59.70; H, 4.93.

(η^8-α,α-Dideutero-4-phenylbutene-1)dicarbonylchromium (37)

The alpha hydrogen-deuterium exchange method of Card (66) was followed. A mixture of 0.400 g (1.67 mmole) of (4-phenylbutene-1)tricarbonylchromium (32), 0.22 g of potassium *t*-butoxide and 4.0 ml of dimethylsufoxide-$\underline{d}_6$ was stirred at ambient temperature for 90 min while being purged with nitrogen. The product mixture was poured into 50 ml of water and neutralized with saturated ammonium chloride. The turbid mixture was extracted twice with 20-ml portions of ether. The combined ether extract was washed with 50 ml of water, dried ($MgSO_4$), filtered and the ether was removed leaving a yellow oil, (η^6-α,α-dideutero-4-phenylbutene-1)tricarbonylchromium

(0.359 g). A solution of 0.300 g of the yellow oil in 200 ml of ether was irradiated (> 290 nm) for 65 min. Removal of the ether gave 0.120 g (0.496 mmole, 43.5%) of **37**; ir (ether) 1925 (vs) and 1871 (vs) cm^{-1}; nmr (acetone-*d*$_6$) δ 5.86-5.52 (m, 3, ArH), 5.10 (d, J = 6.0 Hz, 1, *o*-ArH), 4.66 (t, J = 6.0 Hz, 1, *m*-ArH), 3.76-3.42 (m, 1, $H_2C=C\underline{H}-$), 3.02-2.66 (m, 2, $-C\underline{H}_2CH=CH_2$), 2.80 (d, J = 13.0 Hz, 1, *trans*-$H\underline{H}C=CH-$) and 1.62 (d, J = 8.1 Hz, 1, *cis*-$H\underline{H}C-CH-$); mass spectrum (70 eV) m/e (rel. intensity) 243 (14.7), 242 (47.6) parent ion, 214 (3.32), 186 (100), 93 (47.0) and 91 (4.43).

(η^8-5-Phenylpentene-1)dicarbonylchromium (**36**)

A solution of 0.220 g (0.780 mmole) of (5-phenylpentene-1)-tricarbonylchromium (**33**) in 200 ml of ether was irradiated (> 290 nm) for 70 min. The color of the solution changed from straw to turbid-orange. The solvent was removed from the product mixture and the orange residue was taken up in 20 ml of pentane. The volume of the pentane solution was reduced to about 10 ml and cooling gave 0.0670 g (0.264 mmole, 34%) of **36**: mp (decompn) 80°; ir (ether) 1918 (vs) and 1866 (vs) cm^{-1}; nmr (acetone-*d*$_6$) δ 5.95-5.45 (m, 2, ArH), 5.22 (t, J = 6.0 Hz, 1, *m*-ArH), 4.94 (d, J = 6.0 Hz, 1, *o*-ArH), 4.50 (d, J = 6.0 Hz, 1, *o*-ArH), 3.20-2.58 (m, 1, $H_2C=C\underline{H}-$), 2.30 (d, J = 13.1 Hz, 1, *trans*-$H\underline{H}C=CH-$), 2.60-1.10 (m, 6, $-CH_2CH_2CH_2-$) and 1.59 (d, J = 8.3 Hz, *cis*-$H\underline{H}C=CH-$); mass spectrum (70 eV) m/e (rel. intensity) 255 (0.103), 254 (0.513) parent ion, 198 (1.28), 146 (2.18) and 91 (100). *Exact mass*. Calcd for $C_{13}H_{14}CrO_2$, 254.0399; found, 254.0419 ± .004. *Anal*. Calcd for $C_{13}H_{14}CrO_2$; C, 61.40; H, 5.56. Found: C, 61.20; H, 5.41.

(η^8-Allyl phenyl ether)dicarbonylchromium (**43**)

A solution of 0.200 g (0.741 mmole) of (allyl phenyl ether)tricarbonylchromium (**39**) in 200 ml of ether was irradiated (> 290 nm) for 105 min. During the irradiation, the color of the solution changed from yellow to dark-orange. The ether was removed and the orange residue was taken up in 10 ml of pentane. Cooling gave 0.0710 g (0.294 mmole, 40%) of **43**: mp (decompn) 80-84°; ir (ether) 1937 (vs) and 1883 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.12-5.88 (m, 2, ArH), 5.59 (t, J = 6 Hz, 1, *m*-ArH), 5.19-4.95 (m, 2, ArH), 4.83-4.58 (m, 2, $-C\underline{H}_2CH=CH_2$), 4.00-3.68 (m, 1, $-\underline{H}C=CH_2$), 2.87 (d, J = 13 Hz, 1, *trans*-$HC=C\underline{H}H$) and 1.85 (d, J = 9 Hz, 1, *cis*-$HC=CH\underline{H}$); mass spectrum (70 eV) m/e (rel. intensity) 243 (5.71, 242 (15.7) parent ion, 214 (8.55), 186 (21.4), 145 (31.4), and 94 (100). *Exact mass*. Calcd for $C_{11}H_{10}CrO_3$, 242.0035; found, 242.0031 ± .001. *Anal*. Calcd for $C_{11}H_{10}CrO_3$: C, 54.54; H, 4.17. Found: C, 54.32; H, 4.05.

(η^8-Allyl 3-tolyl ether)dicarbonylchromium (**44**)

A solution of 0.10 g of (allyl 3-tolyl ether)tricarbonylchromium (0.100 g, 0.352 mmole) in 100 ml of ether was irradiated using light of wavelength > 290 nm for 90 min. During the reaction the color changed from clear straw to turbid-orange. The product mixture was filtered and the solvent was removed (vacuum rotary evaporation). The orange residue was dissolved in five ml of pentane and refrigeration gave 0.044 g (0.17 mmole, 48%) of **44**: mp (decompn) 78°; ir (ether) 1928 (vs), 1876 (vs) cm^{-1}; nmr (acetone-$\underline{d}_6$) δ 6.06-5.70 (m, 1.5, ArH), 5.60 (t, J = 6.2 Hz, 0.56, ArH), 5.20-4.45 (m, 4.46, ArH and $-CH_2-$), 3.92-3.55 (m, 1, $-C\underline{H}=CH_2$) 2.80 (d, J = 12.0 Hz, 0.41, *trans*-$CH=C\underline{H}H$), 2.62 (d, J = 12.0 Hz, 0.59, *trans*-$CH=CH\underline{H}$), 2.43 (s, 1.8, $-CH_3$), 2.34 (s, 1.2, $-CH_3$), 1.87 (d, J = 9.0 Hz, 0.41, *cis*-$CH=C\underline{H}H$) and 1.75 (d, J = 9.0 Hz, 0.59, *cis*-$CH=CH\underline{H}$);[1] mass spectrum (70 eV) m/e (rel. intensity) 257 (5.0), 256 (22.3) parent ion, 228 (3.85) 200 (4.15), 159 (100) and 108 (28.4). *Exact mass*. Calcd for $C_{12}H_{12}CrO_3$, 256.0185; found, 256.0185 ± 0.0013.

(η^8-Allyl 3,5-xylyl ether)dicarbonylchromium (**45**)

A solution of (allyl 3,5-xylyl ether)tricarbonylchromium (**41**) (0.100 g, 0.355 mmole) in 100 ml of ether was irradiated with light of wavelength > 290 nm for 105 min. During the reaction the color and appearance of the solution changed from clear pale yellow to turbid orange-yellow. The product mixture was filtered and the solvent was removed (vacuum rotary evaporation). The orange residue was dissolved in 10 ml of pentane and cooled to yield 0.042 g (0.156 mmole, 47%) of **45**: mp (decompn) 86-

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[1] The mixture of diastereomers as indicated by the nmr spectrum could not be separated by fractional crystallization.

89°; ir (ether) 1924 (vs) and 1869 (vs) cm^{-1}; nmr (C_6D_6) δ 5.08 (s, 1, *o*-ArH), 4.60-4.30 (m, 2, -CH_2-), 4.18 (s, 1, *o*-ArH), 3.70 (s, 1, *p*-ArH), 3.70-3.36 (m, 1, -C$\underline{H}$=CH_2), 2.60 (d, J = 12.0 Hz, 1, *trans*-CH=C$\underline{H}$H), 1.98 (s, 3, -CH_3), 1.88 (d, J = 9.0 Hz, 1, *cis*-CH=C$\underline{H}$H) and 1.82 (s, 3, -CH_3); mass spectrum (70 eV) m/e (rel. intensity) 271 (6.76), 270 (22.2) parent ion, 242 (3.38), 214 (53.3), 173 (100) and 122 (31.1). *Exact mass*. Calcd for $C_{13}H_{14}CrO_3$, 270.0348; found, 270.0345 ± 0.0014.

(η^8-Benzyl vinyl ether)dicarbonylchromium (**46**)

(Benzyl vinyl ether)tricarbonylchromium (**38**) (0.100 g, 0.370 mmole) in 100 ml of ether was irradiated (> 290 nm) for 90 min. During the photolysis the solution changed from clear-yellow to turbid-orange. After filtration, the ether was removed and the red oil was taken up in 10 ml of pentane. Refrigeration gave 0.150 g (0.062 mmole, 17%) of (η^8-benzyl vinyl ether)tricarbonylchromium: mp (decompn) 51°; ir (ether) 1928 (vs) and 1878 (vs) cm^{-1}; nmr;[1] mass spectrum (70 eV) m/e (rel intensity) 243 (2.00), 242 (6.68) parent ion, 186 (15.6), 91 (100) and 52 (37.7). *Exact mass*. Calcd for $C_{11}H_{10}CrO_3$, 242.0035; found, 242.0029 ± .0012.

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[1] A satisfactory nmr spectrum was not obtained on this complex.

(2-Phenylethylamine)dicarbonylchromium (**52**)

A solution of 0.010 g of (2-phenylethylamine)tricarbonylchromium (**51**) in 10 ml of ether was irradiated (> 290 nm) for 25 min. The reaction was followed by ir and revealed the formation of two very strong bands of **52** at 1890 and 1833 cm^{-1}; also, a color change was noted from straw to red. When the solvent was removed by rotary evaporation at reduced pressure the red complex decomposed to a grey-green material which was insoluble in organic solvents.

(3-Phenylpropylamine)dicarbonylchromium (**50**)

(3-Phenylpropylamine)tricarbonylchromium (**49**) (0.100 g, 0.369 mmole) in 100 ml of ether was irradiated (> 290 nm) for 45 min. During the reaction the color of the solution changed from straw to red. The solution volume of the product mixture was reduced to about 10 ml by vacuum rotary evaporation and an equal volume of pentane was added; cooling gave 0.035 g (0.114 mmole, 39%) of **50**: mp (decompn) 138°; ir (ether) 1888 (vs) and 1832 (vs) cm^{-1}; nmr (acetone-d_6) δ 5.04 (d, J = 6 Hz, 2, *o*-ArH), 4.37 (t, J = 6 Hz, 2, *m*-ArH), 3.98-3.68 (m, 3, -C*H*$_2$NH$_2$ and *p*-ArH), 2.52 (t, J = 7 Hz, 2, -NH$_2$) and 2.10-1.49 (m, 4, ArCH$_2$CH$_2$-).

Attempted Preparation of Arene-chelate Complexes

Photolysis of *syn*-(benzobicyclo[2.2.2]octadiene)tricarbonylchromium (**29**)

Irradiation of .003 M - .005 M solution of **29** in ether using photolysis conditions described (> 290 nm or 350 nm light in separate experiments) gave decomposition of the complex within one hr as indicated by the formation of a grey-green precipitate and the disappearance of the band at 1890 cm^{-1} in the infrared spectrum.

Photolysis of (benzyl acrylate)tricarbonylchromium (**42**), (1,4-dihydronaphthalene)tricarbonylchromium (**30**), (6-phenylhexene-1)tricarbonylchromium (**34**) and (3-phenylpropene)tricarbonylchromium (**31**)

Ether solutions (.003 M to .005 M) of these complexes were irradiated with light > 290 nm and in separate experiments with light of 350 nm. Decomposition was observed in each experiment as indicated by the appearance of a grey-green precipitate in clear supernatant liquid.

Photolysis of (4-phenylbutylamine)tricarbonylchromium (**53**)

A solution of 0.05 g of **53** in 50 ml of ether was irradiated (> 290 nm) for 15 min. Within that time the complex decomposed as indicated by the development of a grey-green precipitate in a clear supernatant liquid.

Photolysis of (1,3-diallyloxybenzene)tricarbonylchromium (54)

A solution of 0.050 g of 54 in 50 ml of ether was irradiated (> 290 nm) for five hr. A color change from pale yellow to yellow-orange was observed during the first hr of the reaction; but the color faded gradually during the remaining four hr. The ir spectrum of the solution showed a graduate formation of two bands at 1930 and 1875 cm^{-1} with a simultaneous disappearance of the bands of 54 at 1933 and 1895 cm^{-1}. No other new ir bands were seen in the region of 2200 to 1700 cm^{-1}.

Photolysis of (1,3,5-trihomoallylbenzene)tricarbonylchromium (55)

A solution of 0.100 g of 55 in 100 ml of ether was irradiated for 3.5 hr. During the first 1.5 hr of the irradiation a color change was observed from pale yellow to orange. From 1.5 hr to 3.5 hr the orange color faded to colorless and a grey-green precipitate formed. The change in the ir spectrum was from two bands at 1960 and 1895 cm^{-1} to two strong bands at 1914 and 1862 cm^{-1} during the first 1.5 hr. The bands at 1914 and 1862 cm^{-1} gradually decreased and no new bands appeared in the region of 2200 to 1700 cm^{-1}.

Reactions of Arene-chelate Complexes

Decomplexation of (η^6-benzobicyclo[2.2.1]heptadiene)dicarbonylchromium (25) with Cerium(IV)

The method of Trahanovsky and Card was followed (67). To a solution of 0.030 g of 25 in 20 ml of ether 20-40 drops of cerium(IV) were added (1:1 acetonitrile to 1.0 M ceric ammonium nitrate). The mixture was allowed to stand for about 10 min until the organic phase was nearly colorless at which time the phases were separated. The ethereal solution was washed with three 50-ml portions of water, dried ($MgSO_4$), filtered and the ether was removed by distillation (final traces by rotary evaporation at reduced pressure). The standard (10.0 mg of tetrachloroethane) was added to the residue and the mixture was dissolved in one ml of carbon tetrachloride for nmr analysis and gave 42% of benzobicyclo[2.2.1]heptadiene.[1]

(4-Phenylbutene-1)(triphenylphosphine)dicarbonylchromium (58)

A mixture of .0146 g of (η^6-4-phenylbutene-1)dicarbonylchromium (0.0608 mmole), 0.0165 g (0.0630 mmole) of triphenylphosphine (0.1 ml of a 0.165 g/ml PPh_3-C_6D_6 solution) and 0.3 ml of benzene-d_6 was allowed to react in a nmr tube for

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[1] The nmr spectrum exactly matched that of known benzobicyclo[2.2.1]heptadiene.

11 days at ambient temperature. The reaction was followed by nmr and at the end of 11 days the product mixture was rinsed through a filter with 10 ml of ether. The solvent was removed from the filtrate leaving a yellow oil which was dissolved in five ml of pentane. Refrigeration produced an orange solid. The supernatant was decanted from the solid (**58**) which melted as the container was allowed to warm to room temperature. The final traces of pentane were removed by rotary evaporation and gave 0.0205 g (0.0408 mmole, 67%) of **58**: ir ($CHCl_3$) 1890 (vs) and 1830 (vs) cm^{-1}; nmr (C_6D_6) δ 7.90-6.60 (m, 15, P-$C_6\underline{H}_5$), 5.84-5.30 (m, 1, -$C\underline{H}=CH_2$), 5.10-4.00 (m, 7, -$CH=C\underline{H}_2$ and ArH) and 2.60-1.76 (m, 4, -CH_2CH_2-); mass spectrum (12 eV) m/e (rel. intensity) 503 (6.23), 502 (11.3) parent ion, 446 (21.3), 314 (8.72) and 262 (100). Exact mass. Calcd for $C_{30}H_{27}CrO_2P$, 502.11538; found, 502.11484 ± 0.0025.

Reaction of (η^8-allyl 3,5-xylyl ether)dicarbonylchromium (**45**) with carbon monoxide

Carbon monoxide gas was bubbled into a solution of five mg of **45** and two ml of benzene. The reaction was allowed to proceed overnight. The ir spectrum of the product mixture was identical to that of (allyl 3,5-xylyl ether)tricarbonylchromium (**41**) and no ir carbonyl absorptions of **45** were present.

(π-Allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) from the reaction of (η^6-allyl phenyl ether)dicarbonylchromium (43) with triphenylphosphine

A solution of 0.220 g (0.909 mmole) of (η^6-allyl phenyl ether)dicarbonylchromium, 0.20 g (0.761 mmole) of triphenylphosphine and 10 ml of benzene was stirred under nitrogen at ambient temperature for 93 hr. The product mixture showed some decomposition as indicated by an insoluble grey-green precipitate. The mixture was rinsed into a separatory funnel with 50 ml of ether where the ethereal solution was extracted with two 50-ml portions of water. The combined, orange aqueous phase was subjected to rotary evaporation at reduced pressure providing an orange solid. This material was dissolved in 50 ml of benzene and the solution was dried (molecular sieves), filtered and the solvent was removed (rotary evaporation) yielding 0.0588 g (0.243 mmole, 27%) of 61 as an orange crystalline solid: mp (decompn) 115°; ir ($CHCl_3$) 2875 (s), 1972 (vs), 1909 (vs) and 1582 (vs) cm^{-1}; ir (THF) 1957 (vs), 1899 (vs) and 1597 (s) cm^{-1}; nmr (acetone-d_6) δ 6.13-5.77 (m, 3), 4.73 (d, $J = 7.0$ Hz, 2, -CHCOCH-), 4.70-4.52 (m, 1, π-allyl X portion of A_2M_2X), 3.46 (d, $J = 7.0$ Hz, 2, π-allyl M_2 portion of A_2M_2X) and 1.39 (d, $J = 12.0$ Hz, 2, π-allyl A_2 portion of A_2M_2X).[1] Anal. Calcd for $C_{11}H_{10}CrO_3$: C, 54.54; H, 4.17.

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[1] The nmr spectrum was unchanged at temperatures as low as -50°.

Found: C, 54.19; H, 4.16. Molecular weight: Calcd, 242; found, 281.

(π-Allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) from the reaction of (η^8-allyl phenyl ether)dicarbonylchromium (43) with boron trifluoride and subsequent treatment with diisopropylamine

(η^8-Allyl phenyl ether)dicarbonylchromium (0.0450 g, 0.186 mmole) in 3.0 ml of benzene under nitrogen received 0.10 ml of boron trifluoride etherate. A red precipitate was was observed immediately. The solid was isolated by suction filtration and washed with benzene producing 0.0480 g (0.155 mmole, 83%) of (62) the boron trifluoride adduct of 61 as an orange solid: mp (decompn) 140°; ir (THF) 1978 (vs), 1927 (vs) and 1563 (s) cm^{-1}; nmr (acetone-d_6) δ 6.90-6.50 (m, 2), 6.45-6.21 (m, 2), 5.96 (d, J = 6.5 Hz, 1, $-\mathrm{CH}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-$) 5.20-4.70 (m, 1, π-allyl X portion of A_2M_2X), 3.91 (d, J = 7.5 Hz, 2, π-allyl M_2 portion of A_2M_2X), and 1.36 (d, J = 10.0 Hz, 2, π-allyl A_2 portion of A_2M_2X). Anal. Calcd for $C_{11}H_{10}BCrF_3O_3$: C, 42.61; H, 3.26. Found: C, 39.30; H, 3.50.[1]

Benzene (10.0 ml) was layered over 0.0150 g of the adduct (62) and 0.10 ml of diisopropyl amine was added. The orange color of 61 developed immediately in the benzene solution.

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[1] Possibly the sample was hygroscopic and contained 7.07% water. Calcd: C, 39.60; H, 3.81.

The solution was filtered from the boron trifluoride·diisopropylamine salt and the filtrate was transferred to a separatory funnel where aqueous extraction and work-up was carried out according to that used in the preparation of 61 (page 112) and yielded 0.0055 g (47%) of 61. The ir spectrum in chloroform of the product exactly matched that of previously synthesized 61.

(π-Allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) from reaction of (η^6-allyl 3,5-xylyl ether)dicarbonylchromium (45) with triphenylphosphine

A solution of 0.170 g (0.630 mmole) of 45, 0.20 g (0.760 mmole) of triphenylphosphine and 10 ml of benzene was stirred under nitrogen at ambient temperature for 102 hr. The work-up was identical to that used in the preparation of 61 and produced 0.092 g (0.341 mmole, 54%) of 59 as an orange solid: mp (decompn) 110°; ir ($CHCl_3$) 1960 (vs), 1897 (vs) and 1573 (vs) cm^{-1}; ir (CCl_4) 1958 (vs), 1898 (vs) and 1597 (vs) cm^{-1}; nmr (C_6D_6) δ 4.62 (s, 1), 4.60-4.32 (m, 1, π-allyl X portion of A_2M_2X), 4.19 (s, 2), 3.08 (d, J = 7.2 Hz, 2, π-allyl M_2 portion of A_2M_2X), 1.45 (s, 6, $-CH_3$) and 1.02 (d, J = 11.0 Hz, 2, π-allyl A_2 portion of A_2M_2X); mass spectrum (70 eV) m/e (rel. intensity) 271 (7.68), 270 (18.0) parent ion, 242 (11.8), 214 (78.0), 173 (100) and 122 (98.0). Exact mass. Calcd for $C_{13}H_{14}CrO_3$, 270.03481; found, 270.03417 ± 0.0027. Anal. Calcd for $C_{13}H_{14}CrO_3$: C, 57.77; H, 5.23. Found: C, 57.69; H, 5.34.

(π-Allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) from the reaction of (η^{8}-allyl 3,5-xylyl ether)dicarbonylchromium (45) with triethylamine

In an nmr tube 0.020 g of 45, 0.01 ml of triethylamine and 0.40 ml of benzene-d_6 were mixed. The reaction was followed by nmr and revealed the slow development of the spectrum of 59. After 118 hr the contents of the tube was rinsed into a separatory funnel with 10 ml of ether. The solution was extracted with two 10-ml portions of water. The orange aqueous extract was subjected to vacuum rotary evaporation and yielded 0.0048 g (0.018 mmole, 24%) of 59. The material was dissolved in a small amount of chloroform and the solution was dried with molecular sieves. The ir spectrum of the chloroform solution was identical to that of known 59.

Reaction of (allyl 3,5-xylyl ether)tricarbonylchromium (41) with triphenylphosphine

A solution of *ca* 0.020 g of 41, 0.020 g of triphenylphosphine in 0.40 ml of benzene-d_6 was transferred to an nmr tube. No change was observed in the nmr spectrum of mixture (41 and triphenylphosphine) during a period of six days.

Structure Proof and Reactivity of 6-Oxocyclohexadienyl Metal Complexes

Reaction of (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium (61) with boron trifuoride

A solution of 0.0250 g (0.103 mmole) of 61 in 10 ml of benzene was stirred as 0.10 ml of boron trifluoride etherate was added. A red precipitate appeared immediately and after 10 min was suction filtered. The solid was washed with dry benzene and 0.0180 g (0.058 mmole, 56%) of the boron trifluoride adduct (62) was isolated. The ir spectrum of the product matched exactly that of previously prepared 62.

(π-Allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium hydrochloride (60)

(π-Allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) (0.0178 g, 0.0659 mmole) in 3.0 ml of benzene was stirred and the solution was acidified with hydrochloric acid-ether. After a few minutes of stirring an orange precipitate developed. Isolation by suction filtration gave 0.0190 g (0.0620 mmole, 94%) of 60 as an orange solid: mp (decompn) 148°; ir (KBr) 1976 (vs), 1922 (vs) and 1551 (vs) cm^{-1}; mass spectrum (70 eV) m/e (rel. intensity) 270 (0.645), 214 (100), 173 (3.55) and 121 (3.23). Anal. Calcd for $C_{13}H_{15}ClCrO_3$: C, 50.90; H, 4.94; Cl, 11.56. Found: C, 50.68; H, 5.08; Cl, 11.56.

Reaction of (π-allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium (59) with n-butyl lithium

The temperature of a solution of 0.0200 g of 59 in 10 ml of benzene was maintained at -30° using an ethanol-water, dry ice slush. The solution was stirred under nitrogen and 0.10 ml of n-butyl lithium (1.3 M) was added. The mixture was stirred for 30 min and 1.0 ml of methyl iodide was added. After the mixture was allowed to warm to ambient temperature the stirring was continued for an additional 30 min. The product mixture was poured into 25 ml of water and all the orange color appeared in the aqueous phase. Removal of the water from the aqueous phase (vacuum rotary evaporation) produced 0.011 g of recovered 59 (55%). The nmr spectrum of this material in benzene-d_6 exactly matched that of the starting material.

Reaction of (π-allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium with methyl iodide

A solution of 0.015 g of 59 in 5.0 ml of methyl iodide was allowed to stand under nitrogen at ambient temperature for 18 hr. The ir spectrum of the solution remained unchanged during that time.

SUMMARY

The photochemistry of arene-tricarbonylchromium complexes capable of forming arene-chelate complexes has been examined. Irradiation of dilute ether solutions of the tricarbonylchromium complexes of benzobicyclo[2.2.1]heptadiene (syn isomer), dibenzobicyclo[2.2.2]octatriene (syn isomer), 4-phenylbutene-1, 5-phenylpentene-1, allyl phenyl ether, allyl 3-tolyl ether, allyl 3,5-xylyl ether, benzyl vinyl ether, 2-phenylethylamine and 3-phenylpropylamine has resulted in the formation of the corresponding dicarbonylchromium, arene-chelate complex in each case.

Some limitations of this general method of synthesis have been demonstrated by the photoreactions of arene-tricarbonylchromium complexes which failed to produce arene-chelate complexes. Irradiation of the tricarbonylchromium complexes of benzobicyclo[2.2.2]octadiene (syn isomer), 1,4-dihydronaphthalene, 3-phenylpropene, 6-phenylhexene-1, benzyl acrylate, and 4-phenylbutylamine results in decomposition and has not provided the corresponding arene-chelate complexes.

Physical properties of the arene-chelate complexes have been measured by ^1H nuclear magnetic resonance, infrared spectroscopy, mass spectral analysis, elemental microanalysis and molecular weight determinations. It has been shown that most of the arene-chelate complexes can be stored if kept under nitrogen and that (η^8-allyl 3-tolyl ether)dicarbonyl-

chromium and (η^8-allyl 3,5-xylyl ether)dicarbonylchromium are air stable indefinitely.

Some chemical properties of representative arene-chelate complexes have been investigated. Displacement of the metal-bound carbon-carbon double bond has been shown to occur when (η^8-4-phenylbutene-1)dicarbonylchromium is treated with triphenylphosphine and when (η^8-allyl 3,5-xylyl ether)dicarbonylchromium is treated with carbon monoxide, forming (4-phenylbutene-1)(triphenylphosphine)dicarbonylchromium and (allyl 3,5-xylyl ether)tricarbonylchromium respectively. However, the reactions of (allyl phenyl ether)dicarbonylchromium and (η^8-allyl 3,5-xylyl ether)dicarbonylchromium with triphenylphosphine furnishes (π-allyl)(6-oxocyclohexadienyl)dicarbonylchromium and (π-allyl)(6-oxo-2,4-dimethylcyclohexadienyl)dicarbonylchromium respectively, and has provided a method for the preparation of the new 6-oxocyclohexadienyl metal complexes. The cleavage reaction seems to be facile and has been brought about by triethylamine and boron trifluoride as well as triphenylphosphine.

The structure of the π-allyl, 6-oxocyclohexadienyl complexes has been assigned based on observed physical and chemical properties and the assigned structures have been shown to fit the observed nuclear magnetic resonance, infrared, and mass spectra as well as elemental analysis. Furthermore, the 6-oxocyclohexadienyl complexes have been shown to form stable, isolable salts when treated with either hydrochloric acid or boron trifluoride etherate; but do not react with n-butyl lithium or with methyl iodide. The ketone moiety of the 6-oxocyclohexadienyl ligand has been shown to be responsible for the reactivity of the 6-oxocyclohexadienyl metal complexes, which is analogous to the reactivity of known (cyclopentadienone)tricarbonyliron and (cycloheptatrienone)-tricarbonylchromium.

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