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ARENE—METAL COMPLEXES

VIII*. PREPARATION OF (η^8-ALKENYLBENZENE)DICARBONYLCHROMIUM COMPLEXES

WALTER S. TRAHANOVSKY* and RICHARD A. HALL

Department of Chemistry, Iowa State University of Science and Technology, Ames, Iowa 50010 (U.S.A.)

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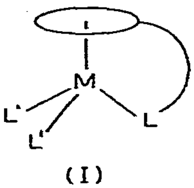
Summary

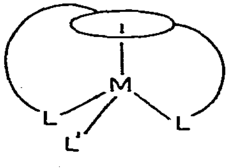
Several (η^8-alkenylbenzene)dicarbonylchromium complexes (arene—chelate complexes) were prepared in fair yield by the photolysis in ether of the tricarbonylchromium complexes of benzonorbornadiene (*syn*-isomer), dibenzobicyclo[2.2.2]octa-2,5,7-triene (*syn*-isomer), 4-phenyl-1-butene, 4-phenyl-1-butene-4,4-d_2, 5-phenyl-1-pentene, allyl phenyl ether, and benzyl vinyl ether. All of these arene—chelate complexes are relatively stable and their IR, NMR, and mass spectral data are presented. Photolysis of the tricarbonylchromium complexes of benzobicyclo[2.2.2]octa-2,5-diene (*syn*-isomer), 1,4-dihydronaphthalene, 3-phenyl-1-propene, 6-phenyl-1-hexene, and benzyl acrylate lead to decomposition and no arene—chelate complexes. It is concluded that this method of preparation of arene—chelate complexes is fairly general but there are some limitations that are apparent from the tricarbonylchromium complexes studied which failed to produce arene—chelate complexes.

Introduction

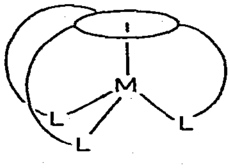
Only a few metal complexes that possess general structure I in which the



(I)



(II)



(III)

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[*] For part VII see ref. 1.

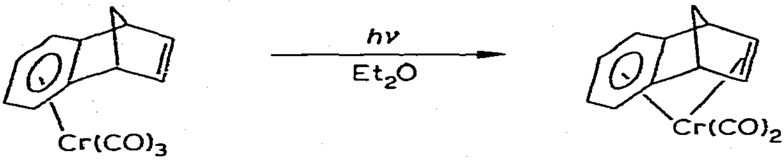
metal is bonded to both a cyclic π system and another functional group which is connected to the cyclic π system by another group of atoms which does not include the metal atom have been reported [2]. These reported complexes are more or less special cases and there are no general synthetic procedures for synthesizing metal complexes that possess structure I. Moreover no complexes have been reported that possess structures II or III. We initiated a program designed to develop general methods of synthesizing complexes that possess structure I, and to eventually learn how to prepare those that possess structures II and III.

In this report we describe a general method for preparing complexes that possess structure I in which the cyclic π system is a benzene ring, M is chromium, L is a carbon—carbon double bond, and L′ is carbon monoxide. The physical properties of several of these arene—chelate chromium complexes are also reported.

Results and discussion

Several arene—chelate chromium complexes were prepared by photolysis of dilute ethereal solutions of the appropriate arene—tricarbonylchromium complexes, which were prepared by standard procedures from the arene and triacetonitriletricarbonylchromium or hexacarbonylchromium [1].

The preparation of (η^8-benzonorbornadiene)dicarbonylchromium (IV) is typical. A 0.004 *M* solution of *syn*-(η^6-benzonorbornadiene)tricarbonylchromium (V) [3] in ether was irradiated for 65 min with a 275 watt sunlamp. During the irradiation the color of the solution changed from yellow to red-orange and the carbonyl region of the infrared spectra of the reaction mixture changed from one strong band at 1891 cm^{-1}[*] to two strong bands at 1937 and 1878 cm^{-1}. Removal of the ether gave a red crystalline material which was recrystallized from hexane to give a 49% yield of IV. The structure of IV was based on its IR, NMR and mass spectra and elemental analysis and molecular weight determination. Of particular interest are the facts that the NMR signal for the alkene protons of IV is 4.0 ppm upfield from the corresponding NMR signal of V and the NMR spectrum of IV indicates that the aromatic ring is still bound to the chromium. The proposed structure for IV was further confirmed by the fact that the ceric ammonium nitrate oxidation of IV gave a 42% yield of the free arene, benzonorbornadiene.



(V) (IV)

In Table 1 are summarized the results of the photolysis of several (alkenylbenzene)tricarbonylchromium complexes. Photolysis of the *syn*-tricarbonyl-

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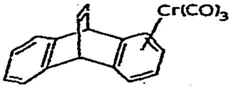
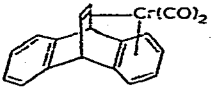
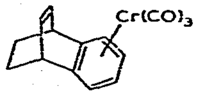
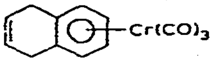
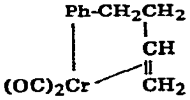
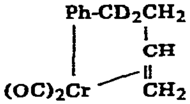
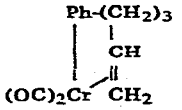
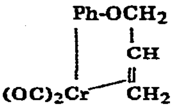
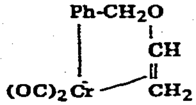
[*] We have found that several arene—tricarbonylchromium complexes give only one intense IR carbonyl band in ether but two intense bands in hexane.

TABLE 1

RESULTS OF THE PHOTOLYSIS OF SEVERAL (ALKENYLBENZENE)TRICARBONYLCHROMIUM COMPLEXES

Tricarbonyl complex	Time of irradiation (min)	Dicarbonyl complex produced	Color of reaction mixture after irradiation	Yield of dicarbonyl complex (%)
V	65	IV	red-orange	49
 (VI)	45	 (XIX)	orange	55
 (VII)	60^a	None	colorless solution with grey-green ppt.	0
 (XVI)	15^b	None	colorless solution with grey-green ppt.	0
$PhCH_2CH=CH_2$ $\vert$ $Cr(CO)_3$ (XVII)		None	turbid $orange^c$	0
$PhCH_2CH_2CH=CH_2$ $\vert$ $Cr(CO)_3$ (VIII)	45	 (XI)	red-orange	53
$PhCD_2CH_2C=CH_2$ $\vert$ $Cr(CO)_3$ (XVIII)	65	 (XX)	red-orange	44
$Ph(CH_2)_3CH=CH_2$ $\vert$ $Cr(CO)_3$ (IX)	70	 (XII)	turbid orange	34
$Ph(CH_2)_4CH=CH_2$ $\vert$ $Cr(CO)_3$ (X)	60^b	None	colorless solution with grey-green ppt.	0
$PhOCH_2CH=CH_2$ $\vert$ $Cr(CO)_3$ (XIII)	105	 (XXI)	dark orange	40
$PhCH_2OCH=CH_2$ $\vert$ $Cr(CO)_3$ (XIV)	90	 (XXII)	turbid orange	17
$PhCH_2OCOCH=CH_2$ $\vert$ $Cr(CO)_3$ (XV)	60^b	None	colorless solution with grey-green ppt.	0

[a] Irradiated with light of wavelength >290 nm (pyrex filter) and with light from 250 nm and 350 nm sources. [b] Also irradiated with light of 350 nm. [c] Solution faded to colorless within minutes.

chromium complex of dibenzobicyclo[2.2.2]octa-2,5,7-triene [1] gave a fair yield of the dicarbonyl complex which had spectral properties similar to that of IV but was slightly more air-sensitive. However, photolysis of *syn*-(benzobicyclo-[2.2.2]octa-2,5-diene)tricarbonylchromium (VII) under a variety of conditions gave no stable complex. The stereochemistry of VII is based on the fact that the NMR signal for the *endo* protons on the ethano bridge are shielded relative to the *exo* protons when the solvent is changed from $CDCl_3$ to benzene-d_6. This kind of solvent effect was noted for several of the stereoisomeric tricarbonylchromium complexes of benzobicyclo[2.2.1]heptane derivatives [3]. Also, the *syn* isomer of the complex of benzonorbornadiene (V) was obtained by the same mode of preparation that was used for VII and so the *syn* isomer is the expected one. We have no good explanation for why a stable arene—chelate complex was not obtained from VII since stable arene—chelate complexes were readily obtained from V and VI and there should be only slight bond angle and length differences for the three bicyclic systems.

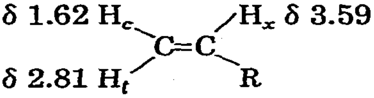
No arene—chelate complex was isolated from the photolysis of the tricarbonylchromium complexes of 1,4-dihydronaphthalene or 3-phenylpropene. However, the turbid-orange color of the reaction mixture from photolysis of the 3-phenylpropene complex suggests that an unstable arene—chelate complex was formed which decomposed before work up.

Relatively stable arene—chelate complexes were obtained in fair yield from the photolysis of the tricarbonylchromium complexes of 4-phenylbutene-1 (VIII) and 5-phenylpentene-1 (IX) but photolysis of the 6-phenylhexene-1 complex (X) gave only decomposition. Evidently photolysis leads to the loss of carbon monoxide [4,5] with the formation of an unstable dicarbonylchromium complex which will decompose if it cannot react with the internal carbon—carbon double bond to form a stable arene—chelate complex. In the case of the hexene derivative, the carbon atom chain which connects the arene and the carbon—carbon double bond must be so long that the rate of formation of the arene—chelate complex is too slow and decomposition of the intermediate takes place. However, the rate of formation of the arene—chelate complex for the slightly shorter pentene and butene chains must be fast enough to compete with decomposition of the intermediate coordinatively unsaturated complex.

Despite the fact that the position of the carbon—carbon double bond relative to the benzene ring is the same for the bicyclic systems which form stable arene—chelate complexes and 3-phenylpropene and 1,4-dihydronaphthalene, namely one carbon atom separates the carbon—carbon double bond from the benzene ring, stable arene—chelate complexes were not obtained from the tricarbonylchromium complexes of the latter two compounds. Presumably these arene—chelate complexes are unstable because too much strain is introduced in going from the uncomplexed to the complexed carbon—carbon double bond. In the bicyclic compounds, a carbon bridge holds the carbon—carbon double bond in a position suitable for complexation and thus less strain is introduced upon complexation of the carbon—carbon double bond.

In order to simplify the analysis of the proton NMR of the arene—chelate complex of 4-phenylbutene-1 (XI), the benzylic protons were replaced with deuterium atoms by photolyzing the α,α-d_2 tricarbonylchromium complex which was obtained by the base-catalyzed hydrogen—deuterium exchange of

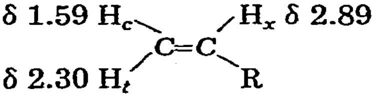
VIII [6]. Analysis of the proton NMR spectra of the d_0 and d_2 arene—chelate complexes indicated that vinyl protons of the complexed carbon—carbon double bond in XI give rise to the following signals:



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

Because of the large chemical shift difference for H_c and H_t, we believe that the carbon—carbon double bond of arene—chelate complex XI is approximately parallel with the benzene ring, not perpendicular to it.

The corresponding NMR data for the 1-pentene arene—chelate complex (XII) are:



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

The greater shielding of H_x in the 1-pentene arene—chelate complex (XII) compared to the 1-butene arene—chelate complex (XI) suggests that the carbon—carbon double bond of XII is closer to the chromium atom.

Arene—chelate complexes were readily obtained from the tricarbonylchromium complexes of the two oxygen containing alkenylbenzenes, allyl phenyl ether (XIII) and benzyl vinyl ether (XIV); however, the arene—chelate complex from XIV was significantly less stable than the one from XIII, which was about as stable as arene—chelate complexes XI and XII. There is evidence that carbon—carbon double bonds which bear electron withdrawing groups form more stable olefin—metal complexes [7] and the instability of the benzyl vinyl ether arene—chelate complex probably reflects the electron donating characteristics of the oxygen atom which is attached to the carbon—carbon double bond. However, photolysis of the tricarbonylchromium complex of benzyl acrylate (XV) gave no arene—chelate complex despite the fact that the carbon—carbon double bond bears an electron-withdrawing carbonyl group. In this case the most stable conformations of XV probably have coplanar carbon—carbon and carbon—oxygen double bonds [8] which result in conformations that are unfavorable for chelation.

Simple non-chelated arene olefin chromium complexes have been prepared [9] but these are much less stable than the arene—chelate complexes.

Many of the non-chelated complexes are very air-sensitive and have not been fully characterized. The increased stability of the chelated versus non-chelated arene olefin chromium complexes is also indicated when one compares the reactivity of the complexes toward displacement of the bound olefin by triphenylphosphine. In the case of (hexamethylbenzene)(cyclopentene)dicarbonylchromium the olefin displacement by triphenylphosphine is rapid and quantitative [9] whereas the reaction of IV under the same conditions is much slower [10].

Conclusions

Stable (η^8-alkenylbenzene)dicarbonylchromium complexes, arene—chelate complexes, can be formed by photolysis of the corresponding arene—tricarbonylchromium complexes if the carbon—carbon double bond is attached to the benzene ring by 2 or 3 methylene groups or a methylene group and an oxygen atom (in either order) or is part of a bicyclic system which causes the carbon—carbon double bond to be in a good position for complexation. Proton NMR spectral evidence suggests that for all of the arene—chelate complexes studied the carbon—carbon double bond is parallel to the benzene ring.

Experimental

Materials and methods

Most equipment has been previously described [1]. Elemental analyses were conducted by Spang Microanalytical Laboratories, Ann Arbor, Michigan, and a molecular weight determination was carried out by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y. An A.E.I. MS-902 mass spectrometer was used for high resolution spectra. Acryloyl chloride, allyl phenyl ether, 5-phenylpentyne-1 and 3-phenylpropene were obtained from Aldrich Chemical Company. 4-Phenylbutene-1 was obtained from Chemical Samples. Hexacarbonylchromium was obtained from Strem. 6-Phenylhexene-1 [11], benzyl vinyl ether [12], benzonorbornadiene [13], benzobicyclo[2.2.2]octa-2,5-diene [14] and 1,4-dihydronaphthalene [15] were synthesized using standard methods. 5-Phenylpentene-1 [16] was synthesized by partial reduction of 5-phenylpentyne-1 [17].

Preparation of (alkenylbenzene)tricarbonylchromium complexes

Method I involves the reaction of the free arene ligands with hexacarbonylchromium in glyme—diglyme solutions at reflux [18]. In the representative synthesis of VIII a mixture of 4.0 ml of 4-phenylbutene-1, 3.0 g (13.6 mmol) of hexacarbonylchromium, 25 ml of glyme and 5 ml of diglyme was heated to reflux for 46 h in a Strohmeier apparatus [19]. 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, hexane/ether) produced a single yellow band which gave 2.78 g of complex VIII (76%) as a yellow oil.

Method II makes use of the reaction of triacetonitriletricarbonylchromium [20] with the free arene ligands. The method is illustrated by the synthesis of VII where a solution of 1.0 g of benzobicyclo[2.2.2]octa-2,5-diene in 20 ml of dioxane was added to triacetonitriletricarbonylchromium (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, pentane/ether) and the long yellow band was collected and gave 0.59 g of VII (31.5%) based on benzobicyclo[2.2.2]octa-2,5-diene.

In Table 2 are presented pertinent data for the (alkenylbenzene)tricarbonylchromium complexes synthesized.

(Benzyl acrylate)tricarbonylchromium (XV). A volume of 0.21 ml (0.23 g, 2.6 mmol) of acryloyl chloride was added at ambient temperature to a stirred solution of 0.79 (2.5 mmol) of pyridine, 0.5 (2.1 mmol) of (benzyl alcohol)tri-

carbonylchromium [3] and 20 ml of ether. The solution was stirred for 1 h under nitrogen. The product mixture was filtered and the solvent was removed leaving 140 mg (78%) of XV as a yellow oil. The pertinent data for XV are summarized in Table 2.

Photolysis conditions. 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 N.E. 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 soil.

Preparation of (η^8-alkenylbenzene)dicarbonylchromium complexes. Dilute ether solutions of the (alkenylbenzene)tricarbonylchromium complexes were irradiated under nitrogen to produce the arene—chelate complexes. The reactions were followed by IR (changes in the C≡O absorption region). The preparation of XI is representative. A solution of 0.10 g (0.37 mmol) of VIII in 100 ml of ether was irradiated with light of wavelength >290 nm for 45 min. The ether was removed from the product mixture and the residue was dissolved in 5 ml of pentane. The solution was placed in a refrigerator and yielded 0.049 g of XI (52.5%). Pertinent data for the (η^8-alkenylbenzene)dicarbonylchromium complexes are presented in Table 3 and the yields, reaction times, and final color for each reaction are shown in Table 1.

(η^8-α,α-Dideutero-4-phenylbutene-1)dicarbonylchromium (XX). A mixture of 0.40 g of VIII, 0.22 g of potassium t-butoxide and 4.0 ml of dimethylsulfoxide was stirred at ambient temperature for 90 min while being purged with nitrogen [6]. The product mixture was poured into 50 ml of water and neutralized with saturated aqueous 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 (XVIII) (0.359 g). A solution of 0.30 g of XVIII in 200 ml of ether was irradiated (>290 nm) for 65 min. Removal of the solvent gave 0.12 g of XX (43.5%). The physical data of XX are presented in Table 3.

Decomplexation of IV with cerium(IV) [21]. To a solution of 30 mg of IV in 20 ml of ether 20-40 drops of cerium(IV) were added (1/1 acetonitrile to 1.0 *M* aqueous 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 1 ml of carbon tetrachloride for NMR analysis and gave 42% of benzonorbornadiene (the NMR spectrum matched that of known benzonorbornadiene).

Photolysis of VII. Irradiation of 0.003 *M*-0.005 *M* solution of VII in ether using photolysis conditions described (>290, 250 or 350 nm) gave decomposition of the complex within one hour as indicated by the formation of a grey-

(continued on p. 82)

TABLE 2

METHODS OF PREPARATION, YIELDS, MELTING POINTS, IR ABSORPTION BANDS, NMR SIGNALS, MASS SPECTRUM SIGNALS AND EXACT MASS MEASUREMENTS OF (ALKENYLBENZENE)TRICARBONYLCHROMIUM COMPLEXES

Tricarbonyl complex	Preparation method	Yield (%)	M.p. (°C)	IR frequency[a] (cm^{-1}) C≡O		Chemical shifts (δ) and assignments[b]	Mass spectrum (70 eV) m/e (relative intensity)	Exact mass of M^+ (m/e)	
								Calcd.	Found
V	II	35	138[c]		1891vs	6.71 (m, 2, HC=CH), 4.77 (AA′BB′ pattern, $\nu_a \sim 5.16$, $\nu_b \sim 4.38$, 4), 3.00 (m, 2, bridgehead H) and 1.49-2.00 (m, 2, CH$_2$)[d,e,f]	279 (8.0), 278 (21) parent ion, 250 (2.0), 222 (10) and 194 (100)		[g]
VI[h]	II								
VII	II	32	150.5[c]		1890vs	6.11 (t, J = 5 Hz, 2, HC=CH), 4.51 (AA′BB′ pattern, $\nu_a \sim 4.74$, $\nu_b \sim 4.28$, 4), 2.90 (m, 2, bridgehead H) and 0.75-1.13 (m, 4, CH$_2$CH$_2$)[d,e]	293 (5.83), 292 (18.3) parent ion, 236 (9.17), 208 (100), 182 (18.8), 130 (22.1) and 52 (39.1)	292.0192	292.0181±0.002[i]
VIII	I	76	[j]	1969s	1901vs	6.10-5.32 (m, 6, ArH and H$_2$C=C$\underline{\text{H}}$), 5.03 (d, J = 17 Hz, 1, *trans*-H$\underline{\text{H}}$C=CH), 4.99 (d, J = 10 Hz, 1, *cis*-H$\underline{\text{H}}$C=CH) and 2.80-2.18 (m, 4, CH$_2$CH$_2$)	269 (5.20), 268 (16.9) parent ion, 240 (0.65), 212 (2.60), 184 (85.8) and 91 (100)	268.0192	268.0189±0.002
IX	I	33	[j]	1970s	1902vs	6.20-5.28 (m, 6, ArH and H$_2$C=C$\underline{\text{H}}$), 5.02 (d, J = 17 Hz, 1, *trans*-H$\underline{\text{H}}$C=CH), 4.94 (d, J = 10 Hz, 1, *cis*-H$\underline{\text{H}}$C=CH), and 2.70-1.20 (m, 6, CH$_2$)	283 (6.04), 282 (20.0) parent ion, 254 (0.377), 226 (0.566), 198 (68.0), 146 (21.1) and 91 (100)	282.0348	282.0347±0.002
X	I	23	[j]	1965w	1900vs	6.22-5.25 (m, 6, ArH and $\underline{\text{H}}$C=CH$_2$), 5.20-4.75 (m, 2, HC=C$\underline{\text{H}_2}$) and 2.60-1.20 (m, 8, CH$_2$)	297 (1.56), 296 (4.55) parent ion, 212 (6.14), 160 (15.6), 91 (100) and 52 (27.3)	296.0505	296.0498±0.0015

XIII	I	34	43.5-45	1967s	1900vs	6.16-4.98 (m, 8, ArH and HC=CH$_2$) and 4.52-4.38 (m, 2, CH$_2$O)	271 (12.0), 270 (41.4) parent ion, 214 (7.68), 186 (94.9), 145 (100), 94 (27.6) and 52 (53.3)	269.9984	269.9986±0.002[k]
XIV	I	16	49.5-50	1968m	1902vs	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$\underline{H}_2$)	271 (1.32), 270 (4.22) parent ion, 214 (1.32), 186 (7.57), 182 (15.0) and 91 (100)	269.9984	269.9982±0.0014[l]
XV	*m*	78	*j*	1968s	1903vs	6.48-5.40 (m, 8, ArH and HC=CH$_2$) and 4.99 (s, 2, ArCH$_2$)	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)	297.9933	297.9935±0.0015
XVI	II	20	113-115		1898vs	5.50-5.20 (s, 2, HC=CH) 4.49 (s, 4, ArH) and 2.62 (s, 4, CH$_2$)[d]	267 (8.7), 266 (30.2) parent ion, 210 (16.8), 182 (16.0) and 52 (100)		*n*
XVII	I	22	*j*	1965w	1892vs	6.00-5.20 (m, 3, HC=CH$_2$), 5.10 (m, 5, ArH) and 3.11 (m, 2, ArCH$_2$)[o]	255 (1.25), 254 (29.0) parent ion, 226 (0.50), 198 (10.1), 170 (100), 118 (40.0) and 91 (25.5)	254.0035	254.0050±0.003

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[a] Ether was used as the solvent. [b] Acetone-d_6 was used as the solvent unless otherwise specified. [c] Decomposition. [d] Benzene-d_6 was used as the solvent. [e] The stereochemistry was assigned *syn*; the NMR spectra of V and VII in chloroform-d_1 show very narrow high-field multiplets (~0.1 ppm) for the alkano bridge hydrogens. Presumably, in benzene-d_6 a solvent molecule, positioned on the face of the arene ring opposite the tricarbonylchromium moiety, shields the endo bridge hydrogens more than the exo bridge hydrogens. [f] The ^{13}C NMR spectrum of this complex recently reported [22] is consistent with the assigned structure. [g] Elemental analysis: Found: C, 60.46; H, 3.71. $C_{14}H_{10}CrO_3$, calcd.: C, 60.44; H, 3.63%. [h] See ref. 1. [i] Elemental analysis: Found: C, 61.46; H, 4.18. $C_{15}H_{12}CrO_3$, calcd.: C, 61.64; H, 4.15%. [j] Oil at 20°C. [k] Elemental analysis: Found: C, 53.28; H, 3.66. $C_{12}H_{10}CrO_4$, calcd.: C, 53.33; H, 3.74%. [l] Elemental analysis: Found: C, 53.41; H, 3.95. $C_{12}H_{10}CrO_4$, calcd.: C, 53.33; H, 3.74%. [m] See Experimental section. [n] Elemental analysis: Found: C, 58.78; H, 3.77. $C_{13}H_{10}CrO_3$, calcd.: C, 58.65; H, 3.79%. [o] Carbon tetrachloride was used as the solvent.

TABLE 3

MELTING POINTS, IR ABSORPTION BANDS, NMR SIGNALS, MASS SPECTRUM SIGNALS AND EXACT MASS MEASUREMENTS OF (η^8-ALKENYLBENZENE)DICARBONYLCHROMIUM COMPLEXES

Dicarbonyl complex	M.p. (dec.) (°C)	IR frequency[a] (cm^{-1}) C≡O		Chemical shifts (δ) and assignments[b]	Mass spectrum (70 eV) m/e (relative intensity)	Exact mass of M^+ (m/e)	
						Calcd.	Found
IV	73	1937vs	1878vs	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)[c,d]	251 (12,0), 250 (43,0) parent ion, 222 (4,0), 194 (52,0) and 52 (100)	250,0086	250,0081±0,0013[e]
XI	74	1925vs	1871vs	5,84-5,55 (m, 3, ArH), 5,09 (d, *J* = 6 Hz, 1, *o*-ArH), 4,64 (t, *J* = 6 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*-$H\underline{H}C{=}CH$)	241 (9,51), 240 (34,3) parent ion, 212 (2,38), 184 (100) and 91 (22,9)	240,0242	240,0248±0,002[f]
XII	80	1918vs	1866vs	5,95-5,45 (m, 2, ArH), 5,22 (t, *J* = 6 Hz, 1, *m*-ArH), 4,94 (d, *J* = 6 Hz, 1, *o*-ArH), 4,50 (d, *J* = 6 Hz, 1, *o*-ArH), 3,20-2,58 (m, 1, $H_2C{=}C\underline{H}$), 2,30 (d, *J* = 13 Hz, 1, *trans*-$H\underline{H}C{=}CH$), 2,60-1,10 (m, 6, CH_2) and 1,59 (d, *J* = 8 Hz, *cis*-$H\underline{H}C{=}CH$)	255 (0,103), 254 (0,513) parent ion, 198 (1,28), 146 (2,18) and 91 (100)	254,0399	254,0410±0,004[g]
XIX	67	1923vs	1872vs	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)[c]	312 (4,0) parent ion, 284 (4,0), 256 (6,0) and 204 (100)[h]	312,0242	312,0250±0,003

XX	74	1925vs	1871vs	5.86-5.52 (m, 3, ArH), 5.10 (d, J = 6 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 1.61 (d, J = 8.1 Hz, 1, *cis*-$\underline{H}HC{=}CH$)	243 (14.7), 242 (47.6) parent ion, 214 (3.32), 186 (100), 93 (47.0) and 91 (4.43)		
XXI	80	1937vs	1883vs	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*-$HC{=}CH\underline{H}$)	243 (5.71), 242 (15.7) parent ion, 214 (8.55), 186 (21.4), 145 (31.4) and 94 (100)	242.0035	242.0031±0.001[i]
XXII	51	1928vs	1878vs	[j]	243 (2.00), 242 (6.68) parent ion, 186 (15.6), 91 (100) and 52 (37.7)	242.0035	242.0029±0.0012

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[a] Ether was used as the solvent. [b] Acetone-d_6 was used as the solvent unless otherwise specified. [c] The solvent was benzene-d_6. [d] See footnote *f* of Table 2. [e] Elemental analysis: Found: C, 62.15; H, 3.99. $C_{13}H_{10}CrO_2$; calcd.: C, 62.40; H, 4.04%. Molecular weight determined osmometrically in benzene: 254. [f] Elemental analysis: Found: C, 59.70; H, 4.93. $C_{12}H_{12}CrO_2$; calcd.: C, 59.99; H, 5.04%. [g] Elemental analysis: Found: C, 61.20; H, 5.41. $C_{13}H_{14}CrO_2$; calcd.: C, 61.40; H, 5.56%. [h] Spectrum obtained at 22 eV. [i] Elemental analysis: Found: C, 54.32; H, 4.05. $C_{11}H_{10}CrO_3$; calcd.: C, 54.54; H, 4.17%. [j] A good NMR spectrum of this complex was not obtained.

green precipitate and the disappearance of the band at 1890 cm^{-1} in the infrared spectrum.

Photolysis of X, XV, and XVI. Ether solutions (0.003 *M* to 0.005 *M*) of these complexes were irradiated with light >290 nm and 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 XVII. Irradiation as described above produced a color change from straw to turbid orange; but the color quickly faded before any physical measurements could be taken. When the irradiation was allowed to proceed for 1 h, decomposition was indicated by the appearance of a grey-green precipitate.

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