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SYNTHESIS AND SPECTRAL STUDY OF CHELATE ALKENYLARENEDICARBONYL COMPLEXES OF Cr, Mo AND W

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Summary

Irradiation of alkenylarene tricarbonyl-chromium, -molybdenum, and -tungsten compounds in which the double bond is separated from the arene moiety by a two- or three-atom bridge results in intramolecular cyclization to give stable chelate alkenylarenedicarbonylmetal complexes. Chelate complexes containing four-atom bridges have low stabilities, and those with monoatomic bridges are not formed at all. Irradiation of styrenetricarbonyl-chromium and -molybdenum leads to dinuclear tricarbonylmetal—dicarbonylmetal complexes. The chelate complexes obtained have been studied by IR, proton NMR, and ^{13}C NMR spectroscopy. The electron density distributions and the stereochemistry of the complexes are discussed. With nonsymmetric arenes, diastereoisomers are formed; the predominant isomers have been isolated in the pure form. According to the proton NMR data the double bond in alkenylarenechromium chelates is parallel of nearly parallel to the arene ring plane.

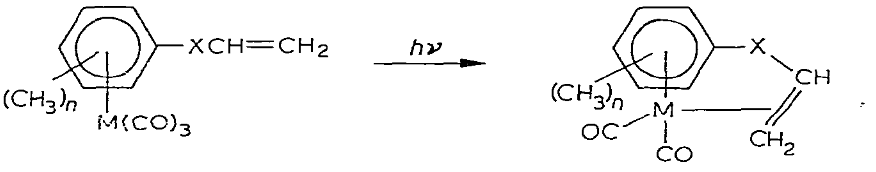
Introduction

Most of the known complexes of the type arene · $M(CO)_2$ · (monoolefin) (M = Cr, Mo and W) are chromium derivatives. Among these complexes of olefinic π-acids such as acrylonitrile, maleic anhydride, maleic and fumaric acids are rather stable [1—4]. Chromium complexes of olefinic π-bases have low stabilities and the only known compounds of this type contain ethylene [5,6], cyclopentene and cycloheptene [6]. Propylene and other alkyl-substituted olefins do not form such complexes. The only reported molybdenum derivative of this type is mesityleneethylenedicarbonylmolybdenum [5,7], while no arene · $W(CO)_2$(olefin) complex is shown.

At the same time, metal complexes of monosubstituted olefins are promising models for spectral studies. The determination of the stereochemistry of the complexes is an important problem; in particular, the relative orientations of the arene and olefinic moieties are of interest. Another point of interest is the electron density distribution in chelate molecules as compared with their non-chelate analogues and also with complexes of the general type arene · $M(CO)_2L$ (L may be CO, PPh_3, etc.). In this work we describe the synthesis and spectra of a number of alkenylarenedicarbonyl-chromium, -molybdenum and -tungsten complexes *.

Results and discussion

Chelate complexes were synthesized in two steps. Firstly, the arene tricarbonylmetal complexes (I) containing a free double bond in the ω-position of the side chain were prepared. Chromium complexes I were obtained as recommended [12]. The molybdenum and tungsten derivatives were previously described by us [13,14] with the exception of the new compound [(3,5-dimethylphenyl)-butene-1]tricarbonylmolybdenum. The second step was the UV irradiation of complexes I. This resulted in the elimination of CO and formation of intramolecular coordination bonds leading to complexes II.



(I) (II)

(M = Cr, Mo, W; n = 0,2,3,5; X = OCH_2, CH_2CH_2, CH_2OCH_2, $(CH_2)_3$, $(CH_2)_4$)

Chelates II were only formed if the bridging groups X contained two or three atoms. Elongation of the bridges by one more atom has a strong destabilizing effect; the fall in stability was most marked with oxygen-containing bridges. The yields of chromium chelates were rather high. All products were crystalline orange or yellow solids. To prove the monomeric structure of the chelates, molecular weights of three chromium complexes II containing allyl phenyl ether, phenylbutene, and phenylpentene as ligands were measured by cryoscopy in benzene. The observed values agreed with the calculated ones (given in parentheses): 236 (242), 233 (240), and 244 (254), respectively.

The conversions of arenetricarbonyl-molybdenum and -tungsten complexes I to chelates II were poor. Bubbling an inert gas through the solutions during irradiation was essential to shift the equilibria to the side of II by removing CO from the reaction zone. Prolonged irradiation gave complete consumption of I and was accompanied by considerable decomposition of chelates II. To obtain the optimum results, the reaction was monitored by IR absorption in the 2000 cm^{-1} region. After the accumulation of sufficient quantities of molybdenum

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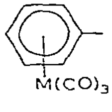
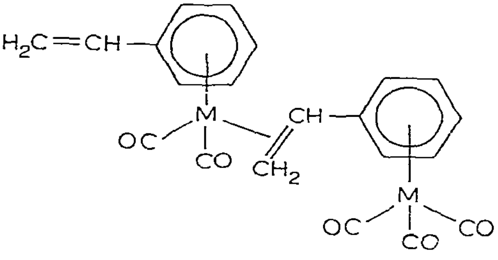
* After our first communication [8] on the synthesis of alkenylarenedicarbonylchromium complexes, similar compounds have been reported by Trahanovsky et al. [9]. These authors have also described the synthesis and ^{13}C NMR spectrum of the related dicarbonylchromium complex with benzonorbornadiene [10] and its reactions with various compounds [11].

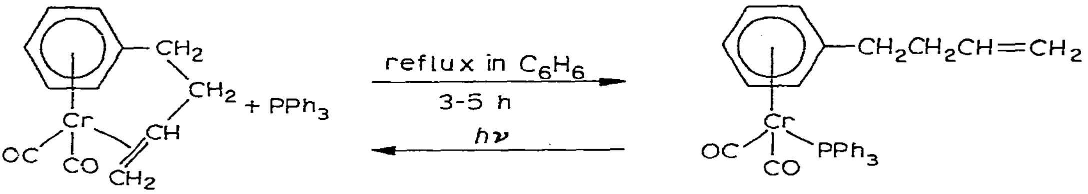
chelates II these were separated from I by crystallization to give the desired products in satisfactory yields. With tungsten, reaction mixtures contained only very small amounts of II even after prolonged (for several days) irradiation. For that reason, arenealkenyltricarbonyltungsten complexes were not isolated and were only characterized by their IR spectra in the 2000 cm^{-1} region. The observed reduction in the rate of substitution of CO by olefinic on going from chromium to molybdenum is in agreement with Strohmeier's data [15] on the photochemical substitution of ^{14}CO for ^{12}CO. For the tungsten arenetricarbonyl complexes, no substitution was reported in that work. The formation of appreciable amounts of tungsten derivatives II may therefore be attributed to the chelate effect. It should be noted that tungsten complexes II reported here provide the first example of complexes of the type arene · W(CO)$_2$L where L is a two-electron ligand.

With a one-unit bridge between the arene and olefinic moieties as in allylbenzene, irradiation of the corresponding tricarbonylchromium derivative resulted in its decomposition. In the absence of bridging groups as in styrene-chromium [16,17] and -molybdenum [14] derivatives, the reaction yields dinuclear complexes III under the same conditions. Both products were isolated as very unstable cherry-coloured solids and were characterized by elemental analysis and IR spectra. The structure of the chromium derivative was substantiated by its reaction with PPh$_3$ which under reflux in benzene for several minutes gave completely styrenetricarbonylchromium and styrenedicarbonyltriphenylphosphinechromium in a ca. 1/1 molar ratio according to the IR spectra. The products were isolated in approximately the same ratio by TLC on silica gel. The formation of complexes III may be explained by the electron-withdrawing action by the substituent  at the double bond.



(III, M = Cr, Mo)

Qualitative comparison of alkenylarenechromium chelates with their nonchelate counterparts shows the former to be far more stable towards heat, oxidation, and towards triphenylphosphine. As mentioned, the double bond in chromium complex III may easily be replaced by PPh$_3$. Substitution of triphenylphosphine for cyclopentene in hexamethylbenzene dicarbonyl chromium occurs under the same conditions [6], whereas with phenylbutene-dicarbonylchromium, the reaction requires refluxing in benzene for several hours, and with the corresponding molybdenum and tungsten derivatives, the substitution does not occur. The initial complex remains intact even after refluxing with PPh_3 in benzene for many hours. It is of interest that UV irradiation



(IV)

of phosphine derivatives IV leads to recovery of the chelates II with displacement of PPh_3 rather than CO.

We have studied the IR, ^1H and ^{13}C NMR spectra of chelate alkenylarene chromium complexes II which are more readily accessible than the molybdenum and tungsten derivatives. For comparison purposes, the spectra of tricarbonylarenechromium complexes I and of the related nonchelate complex, mesityleneethylenedicarbonylchromium [5], have also been measured.

IR spectra. The spectra of $LCr(CO)_3$ (I) and $LCr(CO)_2$ (II) where L is an alkenyl ligand contain two absorption bands in the carbonyl stretching region (see Tables 1—3). A considerable decrease in the $\nu(C{\equiv}O)$ frequency is observed on going from I to II (that is on replacing one CO ligand with an olefinic group). This implies that the combined ($\sigma + \pi$) effect of the double bond generates a higher electron density on the metal compared with that of CO. As with arenetricarbonylmetal I, an increase in the number of electron-donor substituents on the ring shifts $\nu(C{\equiv}O)$ in II to lower frequencies. Similar effects have been reported for arenetricarbonylmetal complexes [18—21] and nonchelate alkenarenedicarbonylchromiums [4,6]. In all complexes I, the A_1 and E vibrations are separated by some 70 cm^{-1}, whereas in II, the frequency difference decreases to ca. 50 cm^{-1}. A similar splitting is observed in the spectrum of mesityleneethylenedicarbonylchromium [5] ($\nu(C{\equiv}O)$ 1864, 1917 cm^{-1}). The variations of $\nu(C{\equiv}O)$ being dependent on the size of the chelate cycle are characteristic for alkenylarenedicarbonylmetal complexes. Thus, $\nu(C{\equiv}O)$ gradually shifts to lower frequencies as the number of bridging CH_2 units increases from two to four in phenylalkenemetal complexes II. A similar pattern is observed for complexes with oxygen-containing bridges, II(2) and II(4), and also for arene complexes containing methyl substituent in the ring (Table 2, 3). The frequency shifts may, at least in part, depend on the steric strain in the chelate cycle. This interpretation finds support in a small (5—10 cm^{-1}) increase in $\nu(C{\equiv}O)$ going from the chromium chelate complexes II to their molybdenum and tungsten analogues (the corresponding frequencies in molybdenum and tungsten complexes are similar). The frequency pattern thus parallels the increase in the metal radius: Cr (1.25 Å) < Mo (1.36 Å) ≈ W (1.37 Å) [22]. Steric strain in chelate cycles increases in the same series [23]. On the other hand, far smaller variations of $\nu(C{\equiv}O)$ are observed in arenetricarbonylmetals in going from Cr to Mo to W (within 1—3 cm^{-1}). Unlike arenetricarbonylchromium complexes I(7)—I(10), compounds II(7)—II(10) show an insignificant dependence of $\nu(C{\equiv}O)$ on the position of methyl substituent in the arene moiety. The frequency shifts

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TABLE 1

YIELDS, MELTING POINTS, IR AND ANALYTICAL DATA ON ARENETRICARBONYLCHROMIUM COMPOUNDS $LCr(CO)_3$ (I)

L in $LCr(CO)_3$	Compound number	Yield (%)	M.p. (°C)	$\nu(C\equiv O)$ (cm^{-1})	Analysis (Found (calcd.) (%))		
					C	H	Cr
$C_6H_5CH_2CH=CH_2$	(1)	(2)	oil	1906	56.55	3.87	20.58
				1977	(56.69)	(3.96)	(20.46)
$C_6H_5OCH_2CH=CH_2$	(2)	56	43—44	1906	53.20	3.77	19.15
				1976	(53.34)	(3.73)	(19.24)
$C_6H_5CH_2CH_2CH=CH_2$	(3)	79	19—20	1906	58.12	4.59	19.47
				1977	(58.21)	(4.51)	(19.39)
$C_6H_5CH_2OCH_2CH=CH_2$	(4)	70	oil	1906	54.81	4.19	18.30
				1977	(54.96)	(4.26)	(18.26)
$C_6H_5(CH_2)_3CH=CH_2$	(5)	76	oil	1906	59.01	4.98	18.59
				1977	(59.28)	(5.03)	(18.55)
$C_6H_5(CH_2)_4CH=CH_2$	(6)	75	oil	1906	60.41	5.40	16.44
				1978	(60.53)	(5.48)	(16.31)
3,5-$(CH_3)_2C_6H_3CH_2CH_2CH=CH_2$	(7)	81	52—53	1899	60.61	5.43	17.62
				1969	(60.80)	(5.44)	(17.55)
3,5-$(CH_3)_2C_6H_3CH_2OCH_2CH=CH_2$	(8)	75	35—36	1899	57.40	5.07	16.36
				1969	(57.69)	(5.16)	(16.65)
2,5-$(CH_3)_2C_6H_3CH_2CH_2CH=CH_2$	(9)	77	48—49	1899	60.69	5.44	17.59
				1968	(60.80)	(5.44)	(17.55)
2,5-$(CH_3)_2C_6H_3CH_2OCH_2CH=CH_2$	(10)	79	oil	1899	57.44	5.10	16.78
				1969	(57.69)	(5.16)	(16.65)
2,4,6-$(CH_3)_3C_6H_2CH_2OCH_2CH=CH_2$	(11)	77	41—42	1896	59.02	5.58	15.97
				1966	(58.64)	(5.59)	(16.34)
2,4,6-$(CH_3)_3C_6H_2(CH_2)_3CH=CH_2$	(12)	71	52—53	1895	62.82	6.07	16.15
				1965	(62.95)	(6.22)	(16.03)
$(CH_3)_5C_6CH_2OCH_2CH=CH_2$	(13)	78	75—76	1883	60.41	6.76	14.46
				1958	(60.44)	(6.83)	(14.39)

TABLE 2

YIELDS, MELTING POINTS, IR AND ANALYTICAL DATA OF ALKENYLDICARBONYLCHROMIUM COMPOUNDS $LCr(CO)_2$ (II)

L in $LCr(CO)_2$	Compound number	Yield (%)	M.p. (°C)	$\nu(C{\equiv}O)$ (cm^{-1})	Analysis (Found (calcd.) (%))		
					C	H	Cr
$C_6H_5OCH_2CH{=}CH_2$	(2)	60	74–75 [b]	1885 1938	54.88 (54.55)	4.21 (4.16)	21.30 (21.47)
$C_6H_5CH_2CH_2CH{=}CH_2$	(3)	65	75–80 [b]	1878 1930	59.73 (60.00)	4.93 (5.03)	21.33 (21.65)
$C_6H_5CH_2OCH_2CH{=}CH_2$	(4)	69	100–105 [b]	1880 1930	56.11 (56.25)	4.68 (4.72)	20.35 (20.29)
$C_6H_5(CH_2)_3CH{=}CH_2$	(5)	68	75–80 [b]	1871 1923	61.68 (61.41)	5.59 (5.55)	20.56 (20.45)
$C_6H_5(CH_2)_4CH{=}CH_2$	(6)	—	—	1866 1920	—	—	—
3,5-$(CH_3)_2C_6H_3CH_2CH_2CH{=}CH_2$	(7)	65	106–108 [b]	1868 1920	62.54 (62.68)	6.10 (6.01)	19.22 (19.38)
3,5-$(CH_3)_2C_6H_3CH_2OCH_2CH{=}CH_2$	(8)	70	116–118	1866 1920	59.00 (59.15)	5.60 (5.67)	18.43 (18.29)
2,5-$(CH_3)_2C_6H_3CH_2CH_2CH{=}CH_2$	(9)	64	72–73	1871 1923	62.80 (62.68)	6.04 (6.01)	19.28 (19.38)
2,5-$(CH_3)_2C_6H_3CH_2OCH_2CH{=}CH_2$	(10)	66	132–134 [c]	1870 1925	58.99 (59.15)	5.54 (5.67)	18.15 (18.29)
2,4,6-$(CH_3)_3C_6H_2CH_2OCH_2CH{=}CH_2$	(11)	84	136–137 [c]	1864 1917	60.03 (60.39)	6.01 (6.08)	17.69 (17.43)
2,4,6-$(CH_3)_3C_6H_2(CH_2)_3CH{=}CH_2$	(12)	62	128–130 [c]	1858 1911	61.03 (61.28)	6.40 (6.49)	16.52 (16.76)
$(CH_3)_5C_6CH_2OCH_2CH{=}CH_2$	(13)	65	150–152 [c]	1856 1909	62.85 (62.69)	6.97 (6.80)	15.45 (15.93)

[a] Notations see Table 1. [b] Decomposition points. [c] Melting with decomposition.

TABLE 3

IR SPECTRA OF CHELATE ALKENYLARENEDICARBONYL-MOLYBDENUM AND -TUNGSTEN COMPLEXES $LM(CO)_2$ (II)

L in $LM(CO)_2$	M = Mo	M = W
$C_6H_5CH_2CH_2CH{=}CH_2$	1883, 1938	1883, 1940
$C_6H_5(CH_2)_3CH{=}CH_2$	1877, 1931	1876, 1930
$3,5\text{-}(CH_3)_2C_6H_3CH_2CH_2CH{=}CH_2$	1871, 1929	1874, 1930

($\Delta\nu$) of 3 cm^{-1} in II(7), II(9) and of 4—5 cm^{-1} in II(8), II(10)) are observed when a CH_3 group is positioned *ortho* to the bridge. The *ortho*-methyl substituent may interact sterically with the olefinic moiety thus causing small changed in the metal—olefin overlap (see below the discussion of the proton NMR spectra).

^{13}C NMR spectra. The ^{13}C NMR method may also be used to gain information about the CO carbon atoms in carbonylsmetals [24,25]. Comparative studies of carbonylmetal complexes by ^{13}C NMR and IR spectra has allowed the authors [26—31] to correlate δ(CO) and k(CO). A general conclusion has been made [24,30] that an increase in the electron density on a metal atom leads to deshielding of the carbonyl carbon atoms because of an increase in the electron-releasing potential of ligands L [32] or a decrease in their electron-withdrawing power [30].

With alkenylarenemetal chelates II, the carbonyl signals show downfield shifts from those in arenetricarbonylchromium complexes [30,33—38] ($\Delta\delta$(CO) 12 ppm with respect to δ(CO) for mesitylene · $Cr(CO)_3$ in CH_2Cl_2 [33]). According to literature data, substitution of PPh_3 for one of the CO groups in arene tricarbonyl compounds results in lesser deshielding of the CO groups ($\Delta\delta$ ca. 7.2 ppm). This observation contradicts he generally accepted view that PPh_3 generates a larger negative charge on the metal than does CO. Thus, the carbonyl ligands in $[C_5H_5Fe(CO)_2L]^+PF_6^-$ are deshielded to a somewhat larger extent when L is PPh_3 than when L = C_2H_4 [31]. With alkenylarene chelates II, deshielding of the carbonyl carbon atoms may in part be due to steric strain in the chelate cycle. Thus, the carbonyl carbon signal in (η^8-benzonorbornadiene)-dicarbonylchromium [10] is shifted downfield from that in the dicarbonylchromium 3,5-dimethylbenzyl allyl ether complex by 3—4 ppm depending on the solvent.

Assignment of the alkenylarene ^{13}C NMR signals was made from comparisons with literature data on coordinated arenes [37and ref. cited therein] and olefins [40 and ref. cited] and on the basis of proton undecoupled ^{13}C—^1H spectra.

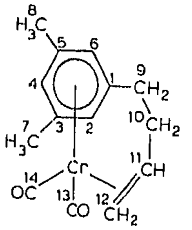
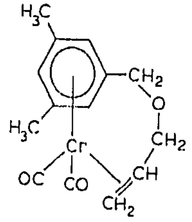
With the 3,5-dimethylphenylbutene-1 complex, substitution of the olefinic ligand for one of the mesitylenetricarbonylchronium CO groups shifts the arene carbon atom signals to higher field, though not as high as on substitution of CO by PPh_3 [39]. At the same time, the C(3) and C(5) nodal carbon atoms in the 3,5-dimethylbenzyl allyl ether derivative are shielded from the corresponding PPh_3 complex and ^{13}CH atoms of the arene ring are generally deshielded from those in mesitylene · $Cr(CO)_3$ [33].

The vinyl carbon atoms undergo upfield shifts of ca. 70 ppm on π-coordination with the metal, the shifts being somewhat larger in the 3,5-dimethylbenzyl allyl

(continued on p. 335)

TABLE 4

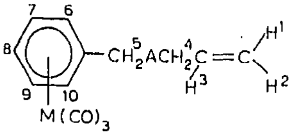
^{13}C NMR SPECTRA OF ALKENYLARENEDICARBONYLCHROMIUM COMPLEXES

Complex	C(1,3,5) [a]	C(2,4,6)	C(7,8)	C(9,10)	C(11)	C(12)	C(13,14)
	107.1 109.9	85.3 90.9 99.2	21.1	29.0 38.6 [b]	67.0	41.5 [b]	
	100.9 105.6	92.1 93.1 97.0 J 173 Hz [c]	20.6 J 129 Hz	68.9 J 143 Hz 71.7 J 147 Hz	59.2 J 163 Hz	34.7 J 159 Hz	246.1 248.1

[a] With reference to TMS. [b] Arbitrary assignment. [c] Spin—spin coupling constants $J(^{13}C{-}^{1}H)$.

TABLE 5

^{1}H NMR DATA OF SOME ARENETRICARBONYL-CHROMIUM, -MOLYBDENUM AND -TUNGSTEN COMPLEXES

 	H(1)	H(2)	H(3)	H(4)	H(5)	H(6)	H(7)	H(8)	H(9)	H(10)
(4)[a] A = O, M = Cr	5.17 d $J_{1,3}$ 17.3 Hz	5.10 d $J_{2,3}$ 9.8 Hz	5.52—6.42 m	3.92 d $J_{3,4}$ 5.2 Hz	3.46	5.25	5.25	5.25	5.25	5.25
(8) A = O, M = Cr	5.30 d $J_{1,3}$ 17.3 Hz	5.23 d $J_{2,3}$ 9.8 Hz	5.62—6.37 m	4.09 d $J_{3,4}$ 5.0 Hz	4.25	5.00	2.22	4.91	2.22	5.00
(10) A = O, M = Cr	5.30 d $J_{1,3}$ 17.3 Hz	5.23 d $J_{2,3}$ 9.8 Hz	5.54—6.45 m	4.08 d $J_{3,4}$ 5.2 Hz	H(5a) 4.04 H(5b) 4.42 $J_{5a,5b}$ 12 Hz	5.17	2.16	5.13 $J_{6,8}$ ~0.5 Hz	5.31 $J_{8,9}$ ~6 Hz	2.11
(11) A = O, M = Cr	5.31 d $J_{1,3}$ 17.1 Hz	5.25 d $J_{2,3}$ 9.7 Hz	5.63—6.37 m	4.07 d $J_{3,4}$ 5.2 Hz	4.17	2.28	4.87	2.20	4.87	2.28
(13) A = O, M = Cr	5.30 d $J_{1,3}$ 17.2 Hz	5.22 d $J_{2,3}$ 9.8 Hz	5.62—6.37 m	4.04 d $J_{3,4}$ 5.2 Hz	4.23	2.22	2.16	2.25	2.16	2.22
(7) A = —, M = Mo	5.09 d $J_{1,3}$ 17.5 Hz	5.03 d $J_{2,3}$ 9.8 Hz	5.43—6.42 m	2.00—2.75 m		5.17	2.26	5.17	2.26	5.17
(7) A = —, M = W	5.09 d $J_{1,3}$ 17.2 Hz	5.03 d $J_{2,3}$ 9.8 Hz	5.26—6.18 m	2.00—2.80 m		5.00	2.41	5.00	2.41	5.00

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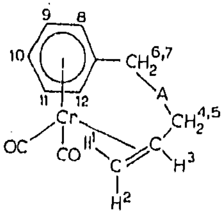
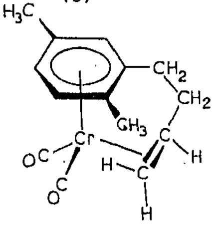
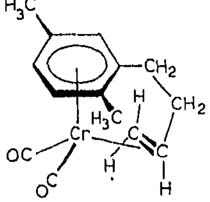
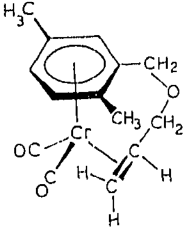
[a] Numbers refer to the groups L as in Table 1.

TABLE 6

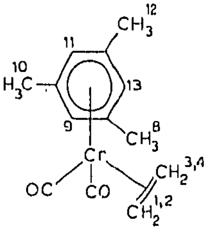
^{1}H NMR DATA OF ALKENYLARENEDICARBONYL-CHROMIUM AND -MOLYBDENUM COMPLEXES LM(CO)$_2$ (II) [a]

	H(1)	H(2)	H(3)	H(4,5)	H(6,7)	H(8)	H(9)	H(10)	H(11)	H(12)
L = (2) A = O, CH$_2^{6,7}$ is absent, M = Cr	2.61 d $J_{1,2}$ ~0 Hz $J_{1,3}$ 12.2 Hz	1.82 d $J_{2,3}$ 8.1 Hz	3.63 m $J_{3(4,5)}$ 3 Hz	In area 4.15—5.70	—	Multiplet in area 4.15—5.70				
L = (3) A = —, M = Cr	2.61 d $J_{1,2}$ ~ 0 Hz $J_{1,3}$ 12 Hz	1.66 d $J_{2,3}$ 7.8 Hz	3.45 m $J_{3(4,5)}$ 3 Hz	2.68 m	2.68 m	4.60 [e] d J 6 Hz	4.33 [e] t	5.45 [e] t	5.35 [e] t	5.20 [e] d
L = (5) A = CH$_2$ (H$_{13,14}$), M = Cr	2.19 d $J_{1,2}$ ~ 0 $J_{1,3}$ 12 Hz	1.65 $J_{2,3}$ 9.8 Hz	2.85 m $J_{3(4,5)}$ 4.5 Hz	With	H$_{13,14}$ 1.85 m	4.05 [e] d J 6 Hz	4.62 [e] t	5.25 [e] t	4.93 [e] t	5.08 [e] d
L = (4) A = O, M = Cr	2.45 d $J_{2,3}$ ~ 0 $J_{1,3}$ 12.8 Hz	1.75 d $J_{2,3}$ 8.3 Hz	3.06 m $J_{3(4,5)}$ 2.5 Hz	3.53 4.13 AB syst. $J_{4,5}$ 13 Hz	3.45 4.33 AB syst. $J_{6,7}$ 12.8 Hz	4.50 [e] J 6.8 Hz	5.03 [e] t	5.61 [e] t	5.28 [e] t	5.23 [e] d
L = (7) A = —, H^{9,11} = 3,5-(CH$_3$)$_2$, M = Cr	2.54 d $J_{1,2}$ ~ 0 Hz $J_{1,3}$ 12.8 Hz	1.55 d $J_{2,3}$ 8.3 Hz	3.40 m $J_{3(4,5)}$ 3 Hz	2.68 m	2.68 m	4.24 [e]	2.33 [e]	5.10 [e]	2.33 [e]	4.45 [e]
L = (8) A = O, M = Cr	2.29 d $J_{1,2}$ ~ 0 Hz $J_{1,3}$ 12 Hz	1.58 d $J_{2,3}$ 9.5 Hz	2.95 m $J_{3(4,5)}$ 3 Hz	3.48 3.96 AB syst. $J_{4,5}$ 13.0 Hz	3.50 4.23 AB syst. $J_{6,7}$ 12 Hz	4.23 [e]	2.15 [e]	5.07 [e]	2.40 [e]	4.83 [e]

(9) 	1.53 d $J_{1,3}$ 12 Hz	1.85 d $J_{2,3}$ 7.6 Hz	2.90 m	2.2 m	2.2 m	2.32^{e}	5.13 $J_{9,10}$ 6 Hz	4.49 $J_{10,12}$ 1.5 Hz	1.97^{e}	5.09
	1.60^{d} d $J_{1,3}$ 12 Hz	1.87 d $J_{2,3}$ 8.2 Hz	3.00^{d} m	2.2^{d} m	2.2^{d} m	$2.35^{d,e}$	5.49^{d} $J_{9,10}$ 6 Hz	4.76^{d} $J_{10,12}$ 1.3 Hz	$2.00^{d,e}$	5.43^{d}
(9) 			3.45^{d} m			$2.59^{d,e}$		4.48^{d} $J_{9,10}$ 6 Hz $J_{10,12}$ 1.3 Hz	$2.28^{d,e}$	4.95^{d}
(10)  A = O	1.29^{d} d $J_{1,2} \sim 0$ Hz $J_{1,3}$ 12 Hz	1.64^{d} d $J_{2,3}$ 8.2 Hz	2.95^{d} m $J_{3(4,5)}$ 2 Hz	3.42^{d} 4.58 AB syst, $J_{4,5}$ 13.5 Hz	4.38^{d} 4.72 AB syst. $J_{6,7}$ 12.5 Hz	$2.18^{d,e}$	5.80^{d} $J_{9,10}$ 6 Hz	5.42^{d} $J_{10,12}$ 1.3 Hz	$1.91^{d,e}$	5.29^{d}
L = **(10)** other diastereomer						$2.43^{d,e}$		$2.30^{d,e}$		
L = **(11)**, A = O	1.27 d $J_{1,2} \sim 0$ Hz $J_{1,3}$ 12.3 Hz	1.80 d $J_{2,3}$ 8 Hz	2.81 m $J_{3(4,5)}$ 2 Hz	3.33 4.14 $J_{6,7}$ 12 Hz	3.73 4.16	2.33^{e}	4.63^{e}	1.85^{e}	5.14^{e}	2.18^{e}
L = **(12)**, A = CH_2 ($H_{13,14}$)	1.35 d $J_{1,2} \sim 0$ Hz, $J_{1,3}$ 12 Hz	2.1 d $J_{2,3}$ 8 Hz	2.73 m	With m 1.85	$H_{13,14}$	2.34^{e}	4.59^{e}	1.75^{e}	5.00^{e}	2.16^{e}

continued

TABLE 6 (continued)

L = (13), A = O	1.05 d $J_{1,2}$ ~ 0 Hz $J_{1,3}$ 12.5 Hz With H(4)	1.63 d $J_{2,3}$ 9.0 Hz	2.55 m $J_{3(4,5)}$ 2.7 Hz	3.45 4.14 AB syst. $J_{4,5}$ 14.7 Hz	4.03 4.31 AB syst. $J_{6,7}$ 13.5 Hz	2.42 [e]	2.38 [e]	1.85 [e]	2.21 [e]	2.31 [e]
	s 1.76			—	—	1.99	4.63 with H(13)	1.99	4.63 with H(13)	1.99
L = (7) M = Mo, A = —	2.61 d $J_{1,2}$ ~ 0 Hz $J_{1,3}$ 12.8 Hz	2.18 d $J_{2,3}$ 7.3 Hz	4.05 m $J_{3(3,5)}$ 3 Hz	2.64 m	2.64 m	4.63 [e]	2.13 [e]	5.03 [e]	2.37 [e]	4.78 [e]

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[a] In CS_2. [b] In ppm downfield from TMS. [c] Notations: d, doublet; t, triplet; m, multiplet; [d] In $(CD_3)_2CO$. [e] May be exchanged.

ether complex; this agrees with the higher stability of this compound. In both complexes, the terminal vinyl carbon signals show larger shifts, possibly because of the smaller carbon—chromium distances [41].

The $^{13}C—^{1}H$ couplings in coordinated olefins and arenes in II differ only slightly from those observed in free olefins [38,40] and arenetricarbonylchromium complexes [37,38,42], respectively.

^{1}H NMR spectra. The proton NMR data on arenetricarbonylmetal complexes I and alkenylarenedicarbonylmetal II are listed in Tables 5 and 6. Complexes I follow established patterns with proton signals showing upfield shifts on coordination [19—21, 42—51], ring proton shieldings decreasing in the order Cr > W > Mo [44,47] which is in agreement with the complex stability pattern, and proton spin—spin coupling constants decreasing on complex formation [19—21,42—51].

On going from I to II, ring proton shielding generally increases. Concerning the arene-methyl groups, the effect of coordination varies from weak shielding to weak deshielding. It is noteworthy that in mesityleneethylenedicarbonylchromium [5], both ring- and arene-CH_3 protons are shielded compared with those in mesitylene · $Cr(CO)_3$. This observation and the IR data confirm the suggestion that the olefinic group $RCH{=}CH_2$ (R = alkyl) increases the electron density on the metal. In the triphenylphosphine complexes arene · $Cr(CO)_2PPh_3$, the effect is even more marked [50].

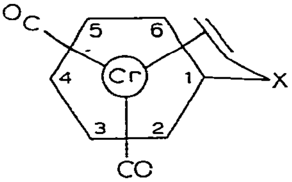
Comparison of the ring proton chemical shifts in I and II is based on averaged values. Ring proton signal assignments and the assignment of arene CH_3 proton signals in II except for the 2,5-dimethylphenylalkene complexes II(**9**) and II(**10**) were not made. In the latter case, the assignments were based on comparisons with the ordering of spin—spin coupling constants in II and I ($J_{ortho} > J_{meta} > J_{para}$) (Table 6). As in other transition metal complexes [52,53], coordination of vinyl groups in complexes II leads to large upfield shifts of the corresponding proton signals. Average vinyl proton signal shifts are on coordination 3.08 ppm in the benzyl allyl ether complex, 3.22 ppm in the 3,5-dimethylbenzyl allyl ether complex, 3.54 ppm in the 2,4,6-trimethylbenzyl allyl ether complex, and 3.75 ppm in the pentamethylbenzyl allyl ether complex, compared to a 3.57 ppm shift for the ethylene proton signals in mesityleneethylenedicarbonylchromium. An increase in the number of electron-donating methyl substituents thus causes a gradual upfield shift of the vinyl proton signal this is indicative of an electron density transfer to the olefinic ligand through the metal atom. The IR spectra show that a similar transfer to the CO ligands occurs. Vicinal proton chemical shift variations parallel those of $\nu(C{\equiv}O)$ being dependent not only on the electron donor ability of the arene moiety but also on the steric strain in the chelate cycle, as may be easily seen from the data on the phenylolefinic complexes II(2)—II(5). The geminal vinyl proton signals will be discussed together with the stereochemistry of complexes II.

Bridging CH_2 group protons in benzyl allyl ether complexes undergo upfield shifts of about 0.2—0.3 ppm on complex formation.

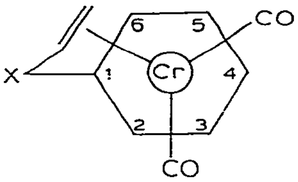
The 2,5-dimethylbenzyl allyl ether complex II has a low solubility in CS_2 and so its proton NMR spectrum has been measured in $(CD_3)_2CO$ solution. The spectrum of the 2,5-dimethylphenylbutene complex has been measured in both solvents. Comparison of the spectra shows that the arene proton chemical shifts depend strongly on the solvent. This phenomenon has already been observed with arenetricarbonylchromium compounds [21,46]. The olefinic proton chemical shifts depend on the solvent to a far smaller extent.

Stereochemistry of alkenylarene chelates II

Coordination of the vinyl group leads to the formation of chiral complexes. All complexes II containing symmetric arenes (i.e. those having a symmetry plane perpendicular to the ring plane) should therefore exist as mixtures of enantiomers II′ and II″.



(II′)

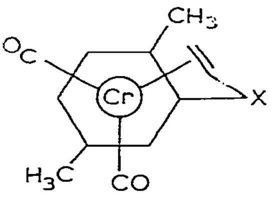


(II″)

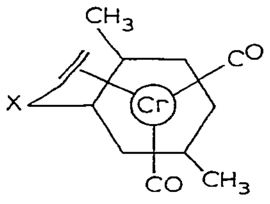
The C(2) and C(6), C(3) and C(5) benzene ring atoms are in diastereomeric environements and may therefore be anisochronous. The same applies to the protons and CH_3 groups attached to these atoms. The CO carbon atoms and bridge CH_2 protons should also be diastereotopic. In fact, all nuclei mentioned show different proton and ^{13}C chemical shifts (Tables 4, 6) with the only exception of CH_3 carbon nuclei in the 3,5-dimethylbenzyl allyl ether and (3,5-dimethylphenyl)butene-1 complexes which are isochronous. In the latter compound, the methyl group protons are also isochronous.

If the arene moiety has no symmetry plane perpendicular to the ring plane as in the 2,5-dimethylphenyl butene-1 and 2,5-dimethylbenzyl allyl ether derivatives, the complexes represent racemic mixtures (complexes I(9) and I(10)). Because of metallocene chirality [54], the side chain methylene protons should be diastereotopic and may be anisochronous [55]. In fact, with the 2,5-dimethylbenzyl allyl ether tricarbonylchromium complex, the benzyl protons are anisochronous (the AB spectrum, Δδ 0.38 ppm, *J* 12 Hz). The allyl-methylene protons are isochronous because they are positioned at large distances from the chiral fragment.

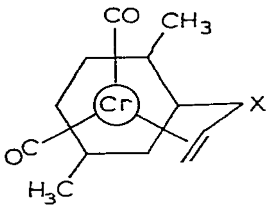
One more chiral fragment appears on going from I(9), I(10) to II(9), II(10). This leads to diastereoisomerism.



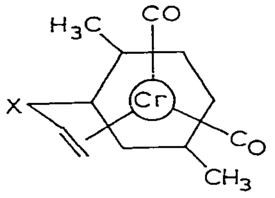
(IIa′)



(IIa″)



(IIb′)

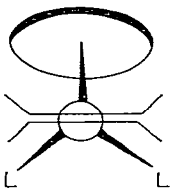


(IIb″)

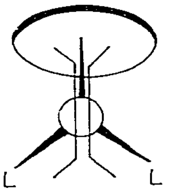
II(9), (X = CH_2CH_2); II(10), (X = CH_2OCH_2)

Compounds IIa′ and IIa″ and also IIb′ and IIb″ represents pairs of enantiomers whereas IIa and IIb are related as diastereoisomers. It should be noted that IIa and IIb are at the same time geometrical isomers because bridging hinders free rotation of the arene and olefinic moieties observed in similar nonbridged compounds. The proton NMR spectra reveal the presence of two types of complexes IIa and IIb; the enantiomer pair IIa′ + IIa″ dominates, the ratio IIa/IIb being equal to ca. 5/1. The racemate (IIa′ + IIa″) may easily be isolated in the pure form by recrystallization.

The orientation of olefinic ligands in the complexes containing planar cyclic ligands is of considerable interest. Two extreme cases are in principle possible:



(A)



(B)

A: the olefinic bond is parallel to the cyclic ligand plane; B: the olefinic ligand is rotated through 90° from its position in A.

The barriers to rotation in such cyclic ligands as cyclopentadienyl and arenes are known to be very low [55—58]. Free rotation has been observed for some arenechromium [56] and cyclopentadienyliron [56] complexes even in the crystal state. With olefinic ligands, the barriers are higher and may often be determined from NMR spectra. In complexes of the type considered here, they amount to, e.g. 7.9 kcal/mol in $[C_5H_5Fe(CO)_2(C_2H_4)]^+$ [60] and 8.4 kcal/mol in $C_5H_5Mn(CO)_2(C_2H_4)$ [61].

A higher stability of conformer B has been predicted for the complex $[C_5H_5Fe(CO)_2(C_2H_4)]^+BF_4^-$ by MO calculations [62]. The more recent NMR study [60] has shown that the predominant conformer is A for C_2H_4, near A with a ca. 10° angle between the double bond and the cyclopentadienyl plane for propylene, and B for isobutylene. Conformer A has the higher stability in $C_5H_5Mn(CO)_2$(olefin) [60]. The X-ray data also show conformers A to dominate [63,64].

The problem of relative orientations of the arene and olefinic ligands in arenedicarbonylmetal complexes has not been studied. We have found that the proton NMR spectrum of mesitylenedicarbonylethylenechromium contains 3 signals with a peak area ratio of 3/4/9. These correspond to arene ring protons, ethylene

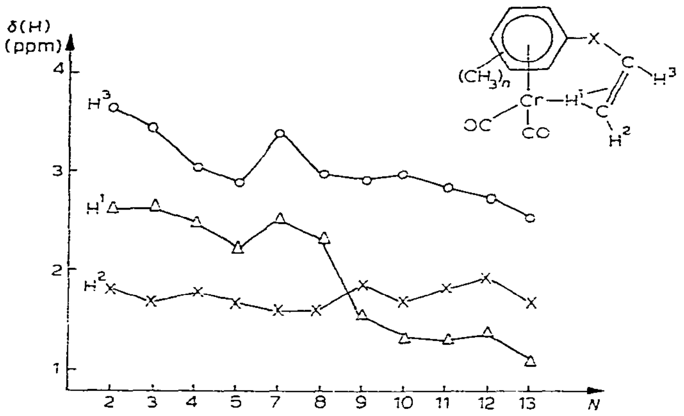


Fig. 1. Vinyl proton signals in the complexes II (*N* is the number under which the complex is included in Table 2).

protons, and CH_3 protons. The fact that ethylene protons appear as a singlet is indicative of either fast rotation about the Cr—ethylene axis or a fast exchange on the NMR time scale. By analogy with isostructural cyclopentadienyl complexes, we suggest rotation of the olefinic ligand to be responsible for the averaging of the olefinic proton signals. Unfortunately, we failed to freeze out the rotation. Some broadening of the ethylene proton signals is observed at —90°C; other peaks, however, exhibit a similar behaviour.

Two orientations of the olefinic group as in A and B are also possible in arene-olefinic chelates II. The occurrence of mixtures of such species can be ruled out on the basis of the NMR evidence. The ^{13}C and ^{1}H NMR spectra reveal the presence of one isomer only. This also follows from the temperature independence of the spectra in the range —70 to +30°C. The presence of bridges in complexes II thus hinders rotations of both arene and olefinic moieties and results in formation of rigid structures.

The large differences between vinyl group geminal protons chemical shifts is indicative of parallel or near parallel orientations of the double bond with respect to the arene cycle plane in complexes II *.

Similar structures were suggested for the complexes $C_5H_5Mn(CO)_2$(olefin) [61] and $[C_5H_5Fe(CO)_2(\text{olefin})]^+BF_4^-$ [60]. The proton NMR spectra provide yet another convincing evidence for the parallel orientation. With arenes containing no substituent positions *ortho* to the bridge, the H(1) shielding varies only slightly (within ca. 0.4 ppm, compounds II(1)—II(6), Fig. 1). The introduction of one or two *ortho* substituents strongly increases the H(1) shielding to the extent that the corresponding signal appears at the higher field than that of H(2) (compounds II(7)—II(11)). Shielding of H(2) varies only significantly in the complexes studied (within 0.35 ppm).

The *ortho*-methyl groups have little effect on H(3) shielding too. The observed large upfield shifts of the H(1) signal on the introduction of *o*-methyl groups may therefore only be explained by direct interaction between H(1) and *o*-CH_3

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* This criterion was suggested by Trahanovsky [9] for alkenylarenechromium complexes.

and displacement of H(1) with respect to the arenedicarbonylchromium fragment having a strong anisotropic shielding action. This explanation is consistent with parallel or near parallel orientations of the double bond relative to the ring plane. Some departure from the parallel orientation may be expected for complexes with two-atomic bridges.

It is of interest that with only one *o*-CH_3 substituent on the ring, the isomers IIa are mostly formed with the olefinic CH_2 group extending to the *ortho*-substituent rather than to the CH group. Such isomers dominate in II(7) and II(8) *.

Experimental

Alkenylarene: allylbenzene [66], phenylbutene-1 [67], phenylpentene-1 [67], phenylhexene-1 [68], and their analogues containing methyl substituents in the ring were obtained by the action of allyl chloride on the corresponding arylalkylmagnesium halide. Phenylallyl ether was obtained according to Claisen [69], benzyl allyl ethers were prepared from the corresponding benzyl halides and $CH_2{=}CHCH_2ONa$ [70]. Arenetricarbonylchromium complexes were synthesized as described in [12], arenetricarbonylmolybdenum ones as described in [13,14], and arenetricarbonyltungsten derivatives following the procedure [14]. Synthesis and isolation of the compounds studied were carried out under an argon atmosphere.

The IR spectra were measured in cyclohexane using an IKS-14A instrument calibrated against DCl. The frequencies were reproducible to within 1 cm^{-1}. The proton NMR spectra were obtained in CS_2 on a Hitachi—Perkin—Elmer R-20 instrument operated at 60 MHz. The solution concentrations were 0.35—0.40 *M*. The temperature dependences were studied with an RYa-2310 spectrometer (60 MHz). The ^{13}C NMR spectra were obtained for solutions in CH_2Cl_2 using a Bruker HX-90 instrument operated at 22.635 MHz.

Chelate chromium alkenylarenedicarbonyl complexes

Complex I (0.1 mmol) was dissolved in 100 ml petroleum ether (b.p. 40—70°C), the solution was irradiated with a PRK-7 mercury arc lamp until the initial complex disappeared ** (5 to 8 h). The red-orange solution was then filtered and the filtrate was evaporated under vacuum until crystallization began. The solution was then cooled with solid CO_2 to give crystalline II. Yields, m.p.'s, and analytical data are listed in Table 2.

[(3,5-Dimethylphenyl)butene-1]tricarbonylmolybdenum

The compound was made from $Py_3Mo(CO)_3$ (0.63 g, 1.5 mmol), (3,5-dimethylphenyl)butene-1 (0.25 g, 1.5 mmol), and $BF_3 \cdot Et_2O$ (0.62 ml, 4.5 mmol) in 50 ml ether as described in [14]. The yield was 65% (0.34 g), m.p. 82—84°C (dec.). IR: $\nu(C{\equiv}O)$ 1900, 1972 cm^{-1}. (Found: C, 52.95; H, 4.68; Mo, 28.11. $C_{15}H_{16}O_3Mo$ calcd.: C, 52.95; H, 4.74; Mo, 28.20%.)

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* The structure of complex II(8) was proved by the X-ray study of the racemate IIa [65].

** Monitored by IR spectroscopy in the region of 2000 cm^{-1}.

[(3,5-Dimethylphenyl)butene-1]dicarbonylmolybdenum

[(3,5-Dimethylphenyl)butene-1]tricarbonylmolybdenum (0.34 g, 1 mmol) was irradiated for 20 h in 150 ml petroleum ether through which argon was bubbled. The reaction mixture was filtered, evaporated to half its initial volume, and maintained at solid CO_2 temperature for 2 days. The precipitate was isolated, dissolved in heptane and frozen out once more. The product was [(3,5-dimethylphenyl)butene-1]dicarbonylmolybdenum, decomposition point 85—90°C. (Found: C, 53.70; H, 5.08; Mo, 30.65. $C_{14}H_{16}O_2Mo$ calcd.: C, 53.85; H, 5.16; Mo, 30.73%.)

Irradiation of styrenetricarbonylchromium

A solution of styrenetricarbonylchromium (0.48 g, 2 mmol) in 100 ml petroleum ether was irradiated for 6 h. The precipitate was separated by decantation, washed with petroleum ether (2 × 10 ml), and dissolved in 10 ml CH_2Cl_2. The solution was filtered into 100 ml petroleum ether and maintained at the solid CO_2 temperature. The precipitate formed was separated, washed with petroleum ether and dried under argon to give (styrenedicarbonylchromium)-styrenetricarbonylchromium (0.123 g, 27%), decomposition point 80—85°C. IR (CH_2Cl_2): ν(CO) 1869, 1886, 1921, 1972 cm^{-1}. (Found: C, 55.35; H, 3.76; Cr, 23.43. $C_{21}H_{16}O_5Cr_2$ calcd.: C, 55.76; H, 3.57; Cr, 22.99%.)

Irradiation of styrenetricarbonylmolybdenum

A solution of styrenetricarbonylmolybdenum (0.28 g, 1 mmol) in 100 ml petroleum ether was UV irradiated for 20 h. The precipitate formed was separated by filtration and recrystallized from toluene/heptane by freezing-out to give the binuclear complex III (0.08 g, 15%), decomposition point 78—83°C. IR (heptane): ν(CO) 1880, 1916, 1937, 1985 cm^{-1}. (Found: C, 46.45; H, 2.90; Mo, 35.40. $C_{21}H_{16}O_5Mo_2$ calcd.: C, 46.68; H, 2.99; Mo, 35.52%.)

Reaction of styrenedicarbonylchromiumstyrenetricarbonylchromium with PPh_3

A solution of complex III (M = Cr) (0.123 g, 0.27 mmol) and PPh_3 (0.15 g, 0.57 mmol) in 10 ml benzene was refluxed for 5 min. During refluxing, the colour of the solution changed from cherry to red. The reaction mixture was evaporated and the residue was chromatographed on silica gel plates using ether/petroleum ether (1/4) as eluent to give styrenetricarbonylchromium (0.05 g, 77%), m.p. 78—79°C from hexane (lit. [16,17] 80—81°C), IR (heptane): ν(CO) 1915, 1980 cm^{-1}, and styrenedicarbonyltriphenylphosphinechromium (0.10 g, 78%), m.p. 149—151°C from hexane, IR (heptane): ν(CO) 1861, 1909 cm^{-1}, proton NMR ($CDCl_3$): $\delta(C_6H_5)$ 4.56—4.87 (5H, m), δ(H(2)) 5.22 (1H, d, J_{23} 10.0 Hz), δ(H(1)) 5.49 (1H, d, J_{13} 17.0 Hz), δ(H(3)) 6.29 (1H, dd), $\delta(Ph_3P)$ 7.23—7.92 (15H, m). (Found: C, 70.98; H, 5.07; P, 6.50; Cr, 10.89. $C_{28}H_{23}O_2PCr$ calcd.: C, 70.88; H, 4.88; P, 6.53; Cr, 10.96%.)

Reaction of phenylbutenedicarbonylchromium with PPh_3

A solution of phenylbutenedicarbonylchromium (0.24 g, 1 mmol) and triphenylphosphine (0.52 g, 2 mmol) in 30 ml benzene was refluxed for 5 h. The solution was then cooled and evaporated under vacuum. The residue was recrystallized from toluene/heptane to give phenylbutenedicarbonyltriphenylphosphinechromium (0.3 g, 60%), m.p. 101—103°C. IR: ν(CO) 1852, 1904 cm^{-1}. (Found: C, 71.66; H, 5.34; P, 6.19; Cr, 10.39. $C_{30}H_{27}O_2PCr$ calcd.: C, 71.70; H, 5.42; P, 6.16; Cr, 10.34%.)

References

1 J.F. Guggenberger and W. Strohmeier, Chem. Ber., 100 (1967) 2807.
2 R.J. Angelici and L. Busettto, Inorg. Chem., 7 (1968) 1935.
3 M. Herberhold and C. Jablonski, J. Organometal. Chem., 14 (1968) 457.
4 M. Herberhold and C. Jablonski, Inorg. Chim. Acta, 7 (1973) 241.
5 E.O. Fischer and P. Kuzel, Z. Naturforsch., B, 16 (1961) 475.
6 W. Strohmeier and H. Hellmann, Chem. Ber., 98 (1965) 1598.
7 M. Herberhold, Metal π-Complexes, Elsevier, Amsterdam, 1972, p. 56 of Russian translation.
8 A.N. Nesmeyanov, M.I. Rybinskaya, V.V. Krivykh and V.S. Kaganovich, J. Organometal. Chem., 93 (1975) C8.
9 W.S. Trahanovsky and R.A. Hall, J. Organometal. Chem., 96 (1975) 71.
10 B.A. Howell and W.S. Trahanovsky, J. Magn. Res., 20 (1975) 141.
11 B.A. Howell and W.S. Trahanovsky, J. Amer. Chem. Soc., 97 (1975) 2136.
12 B. Nichols and M.C. Whiting, J. Chem. Soc., (1959) 551.
13 A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., (1974) 863.
14 A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, J. Organometal. Chem., 102 (1975) 185.
15 W. Strohmeier and D. von Hobe, Z. Naturforsch. B, 18 (1963) 770.
16 M.D. Rausch, G.A. Moser, E.J. Zaiko and A.L. Lipman, J. Organometal. Chem., 23 (1970) 185.
17 G.R. Knox, D.G. Leppard, P.L. Pauson and W.E. Watts, J. Organometal. Chem., 34 (1972) 347.
18 R.D. Fischer, Chem. Ber., 93 (1960) 165.
19 D.A. Brown and J.R. Raju, J. Chem. Soc. A, (1966) 1617.
20 W. McFarlane and S.O. Grim, J. Organometal. Chem., 5 (1966) 147.
21 G. Klopman and K. Noack, Inorg. Chem., 7 (1968) 579.
22 J.A. Campbell, Chemical Systems, San Francisco, 1960, p. 150 of Russ. Trans.
23 D.St.C. Black and A.J. Hartshorn, Coord. Chem. Rev., 9 (1972/1973) 219.
24 L.J. Todd and J.R. Wilkinson, J. Organometal. Chem., 77 (1974) 1.
25 B.E. Mann, Advan. Organometal. Chem., 12 (1974) 135.
26 O.A. Gansow, B.Y. Kimura, G.R. Dobson and R.A. Brown, J. Amer. Chem. Soc., 93 (1971) 5922.
27 G.M. Bodner, S.B. Kahl, K. Bork, B.N. Storhoff, J.E. Wuller and L.J. Todd, Inorg. Chem., 12 (1973) 1071.
28 P.J. Vergamini and N.A. Matwiyoff, Abstr. Rocky Mountain Reg. Meeting Amer. Chem. Soc., June 1972.
29 O.A. Gansow, D.A. Shexnayder and B.Y. Kimura, J. Amer. Chem. Soc., 94 (1972) 3406.
30 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 1335.
31 G.M. Bancroft, K.D. Butler, L.E. Manzer, A. Shaver and J.E.H. Ward, Canad. J. Chem., 52 (1974) 782.
32 P.S. Braterman, D.W. Milne, E.W. Randall and E. Rosenberg, J. Chem. Soc., Dalton Trans., (1973) 1027.
33 B.E. Mann, Chem. Commun., (1971) 976.
34 B.E. Mann, J. Chem. Soc., Dalton Trans., (1973) 2012.
35 L.F. Farnell. E.W. Randall and E. Rosenberg. Chem. Commun., (1971) 1078.
36 A.N. Nesmeyanov, E.I. Fedin, L.A. Fedorov and P.V. Petrovskii, Zh. Strukt. Khim., 13 (1972) 1033.
37 G.M. Bodner and L.J. Todd, Inorg. Chem., 13 (1974) 360.
38 D.J. Thoennes, C.L. Wilkins and W.S. Trahanovsky, J. Magn. Res., 13 (1974) 18.
39 L.A. Fedorov, P.V. Petrovskii, E.I. Fedin, N.K. Baranetskaya, V.I. Zdanovich, V.N. Setkina and D.N. Kursanov, Dokl. Akad. Nauk SSSR, 209 (1973) 404.
40 M.H. Chisholm, H.C. Clark, L.E. Manzer, J.B. Stothers and J.E.H. Ward, J. Amer. Chem. Soc., 97 (1975) 721.
41 D.G. Cooper, G.K. Hamer, J. Powell and W.F. Reinolds, Chem. Commun., (1973) 449.
42 R.V. Emanuel and E.W. Randall, J. Chem. Soc., A, (1969) 3002.
43 T.B. Brill and A.J. Kotlar, Inorg. Chem., 13 (1974) 470.
44 H.P. Fritz and C.G. Kreiter, J. Organometal. Chem., 7 (1967) 427.
45 W. Strohmeier and H. Hellmann, Chem. Ber., 97 (1964) 1877.

46 A. Mangini and F. Taddei, Inorg. Chim. Acta, 2 (1968) 8.

47 J.T. Price and T.S. Sorensen, Canad. J. Chem., 46 (1968) 515.

48 W.R. Jackson, C.H. McMullen, R. Spratt and P. Bladon, J. Organometal. Chem., 3 (1965) 392.

49 G. Segard, B. Roques, C. Pommier and G. Guiochon, Analyt. Chem., 43 (1971) 1146.

50 D.N. Kursanov, V.N. Setkina, P.V. Petrovsky, V.I. Zdanovich, N.K. Baranetskaya and I.D. Rubin, J. Organometal. Chem., 37 (1972) 339.

51 N.J. Gogan and C.S. Davies, J. Organometal. Chem., 39 (1972) 129.

52 M. Tsutsui, M.N. Levy, A. Nakamura, M. Ichikawa and K. Mori, Introduction to Metal π-Complex Chemistry, Plenum Press, New York, 1970.

53 R.G. Kidd and M. Tsutsui (Ed.), Characterisation of Organometallic Compounds, Part II, New York, 1971; R. Kidd, Usp. Khim., 42 (1973) 1943.

54 K. Schlögl, Metallocene Stereochemistry in N.L. Allinger and E.L. Eliel (Eds.), Topics in Stereochemistry, New York, 1967, Vol. 1, p. 48 of Russ transl.

55 K. Mislow and M. Raban, in Ref. 54, Vol. 1, 1967, p. 31 of Russ. transl.

56 C.H. Holm and J.A. Ibers, J. Chem. Phys., 30 (1959) 885.

57 B.P. Roques, C. Segard, S. Combrisson and F. Wehrli, J. Organometal. Chem., 73 (1974) 327.

58 W.R. Jackson, C.F. Pinkombe, J.D. Rae and S. Thapebinkarn, Aust. J. Chem., 28 (1975) 1535.

59 P. Delise, G. Allegra, E.R. Mongnaschi and A. Chirico, J. Chem. Soc. Faraday II, (1975) 207.

60 J.W. Faller and B.V. Johnson, J. Organometal. Chem., 88 (1975) 101.

61 H. Alt, M. Herberhold, C.G. Kreiter and H. Strack, J. Organometal. Chem., 77 (1974) 353.

62 M.L.H. Green and P.L.I. Nagy, J. Organometal. Chem., 1 (1963) 58.

63 M. Ziegler, Z. Anorg. Allgem. Chem., 355 (1967) 12.

64 B. Granoff and R.A. Jakobson, Inorg. Chem., 7 (1968) 2328.

65 Yu.T. Struchkov, V.G. Andrianov, A.N. Nesmeyanov, V.V. Krivykh, V.S. Kaganovich and M.I. Rybinskaya, J. Organometal. Chem., 117 (1976) C81.

66 E.B. Hershberg, Helv. Chim. Acta, 17 (1934) 352.

67 A.P. Kozacik and E.E. Reid, J. Amer. Chem. Soc., 60 (1938) 2436.

68 J. v. Broun, H. Deutsch and A. Schmatloch, Chem. Ber., 45 (1912) 1246.

69 L. Claisen, Ann., 418 (1919) 97.

70 Weygand—Hilgetag, Organisch-chemische Experimentierkunst, Verlag, 1964, p. 333 of Russ. transl.