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INDENYL- AND FLUORENYL-TRANSITION METAL COMPLEXES

I. SYNTHESIS, STRUCTURES, AND REACTIONS OF η^5- AND η^6-DERIVATIVES OF CHROMIUM GROUP METALS

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Summary

The reactions leading to the η^5-fluorenyl- and η^5-indenyl-tricarbonylmetallate anions, η^5-$C_{13}H_9(CO)_3Cr^-$ and η^5-$C_9H_7(CO)_3M^-$ where M stands for Cr, Mo, W have been studied. Deprotonation of (η^6-fluorene)$Cr(CO)_3$ with t-BuOK seemingly proceeds via the corresponding η^6-anionic intermediate which is transformed into the η^5-isomer with a conversion halftime of several minutes. Chromium and molybdenum η^5-anions rearrange on treatment with CH_3COOH to the corresponding η^6-indene and fluorene complexes. Protonation of η^5-C_9H_7-$(CO)_3W^-$ leads to the stable hydride η^5-$C_9H_7(CO)_3WH$. All the anions studied react with $Hg(CN)_2$ to give symmetric organomercury derivatives containing M—Hg bonds (M = Cr, Mo, W). The reactions of η^5-$C_9H_7(CO)_3Cr^-$ and η^5-$C_{13}H_9$-$(CO)_3Cr^-$ with CH_3I proceed via formation of the compounds having an η^5-structure and containing a Cr—CH_3 bond: the product η^5-$C_9H_7(CO)_3CrCH_3$ has been isolated and characterized. The σ-methylchromium derivatives readily undergo thermal rearrangement to the η^6-compounds via transfer of the CH_3 group to the five-membered ring and of the $Cr(CO)_3$ group to the benzene nucleus.

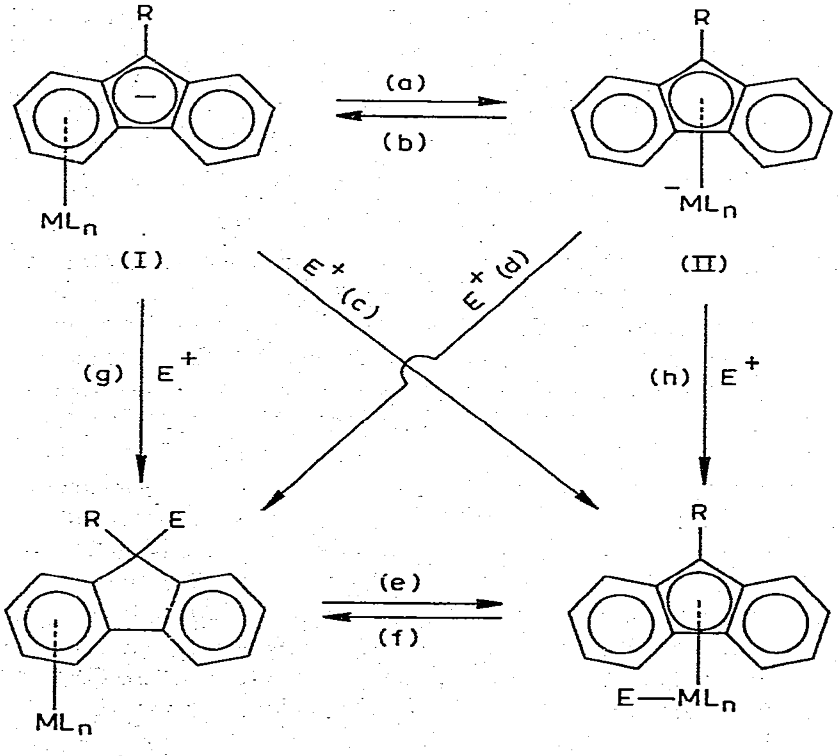
The molybdenum and tungsten anions form stable σ-methyl derivatives in reactions with CH_3I. The possible reversible isomerization processes involving anionic and neutral compounds are considered from mechanistic and stereochemical points of view.

Introduction

Indene, fluorene and the corresponding anions can form several series of organoelement compounds: the η^1-derivatives of transition and non-transition elements, the η^5- and η^6-transition metal complexes, and compounds with the η^3-type metal-to-ligand coordination. Reactions are known which bring about changes in the type of metal-to-ligand bonding in indenyl and fluorenyl transition metal derivatives. Nicholas and co-workers [1] have shown that deprotonation of η^6-fluorenetricarbonylchromium is accompanied by transfer of the $Cr(CO)_3$ moiety to the five-membered ring so that the resulting anion has the η^5-structure. Lee et al. [2] have observed the formation of an η^5-indenyl-η^6-indeneiron cation during the reaction of di-η^5-indenyliron with boron fluoride etherate. The same cation was found by Treichel and Johnson [3] to occur during the protonation of di-η^5-indenyliron with trifluoroacetic acid *.

In all these reactions, only one of two possible isomers is formed and has either the η^5- or the η^6-structure. In general it might be expected that indenyl-

SCHEME 1



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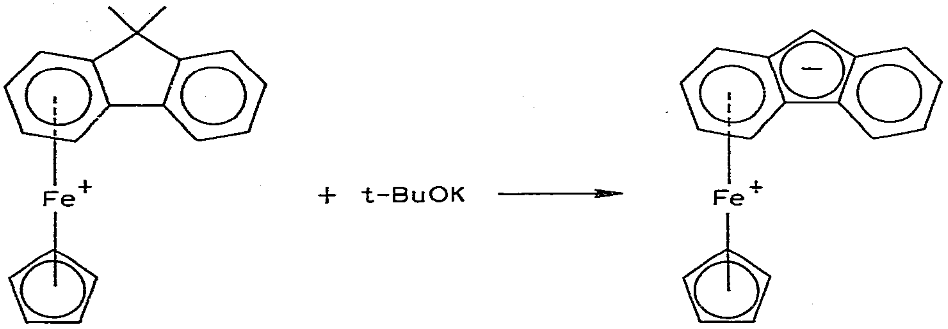
* The latter two of these three reactions may be considered as particular cases of replacement of a cyclopentadienyl ligand with an arene ligand in the iron complexes discovered by one of the present authors (A.N.N.) together with N.A. Vol'kenau and I.N. Bolesova [4,5]. The former reaction exemplifies the reverse process.

and fluorenyl-transition metal derivatives would exist that: (i) have nearly thermodynamically equal η^5- and η^6-forms and (ii) are characterized by low $\eta^5 \rightleftharpoons \eta^6$, interconversion barriers.

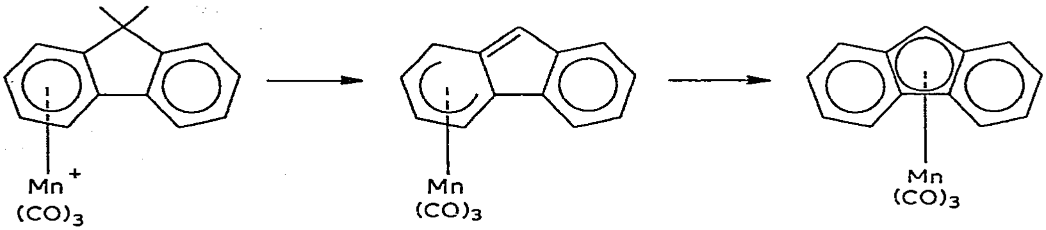
Interconversion (processes a and b) might in principle occur with isomeric anions I and II (Scheme 1) *.

So far, fluorenyl complex anions having only the η^5-structure have been known [1]. Treichel and Johnson [6,7] have however shown recently that the neutral complex VI formed during deprotonation of the η^6-fluorene-η^5-cyclopentadienyliron cation (V) has the η^6-structure and therefore represents a zwitterion.



(V) (VI)

In contrast, deprotonation of the η^6-fluorenetricarbonylmanganese cation (VII) leads eventually to the η^5-derivative IX described earlier by King and Efraty [8], although the reaction proceeds via an intermediate which has been isolated and whose structure can best be described as VIII [9].



(VII) (VIII) (IX)

King [10] has reported the preparation of an η^5-indenyltricarbonylmolybdate anion but no detailed information about the structure and properties of similar anions is available.

We believe that variation of the substituent R in the five-membered ring, the metal atom M and the ligand L can lead to compounds which undergo reversible rearrangements a and b (Scheme 1) and which exist as equilibrium mixtures of I and II. Such rearrangements would represent a novel type of metallotropic tautomerism with an organometallic group attached to a planar aromatic polynuclear ligand shifting from one ring to another along the plane of the π-electronic system.

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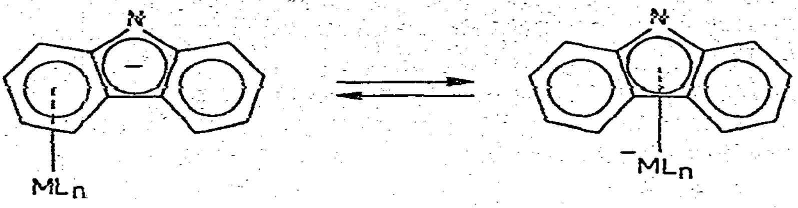
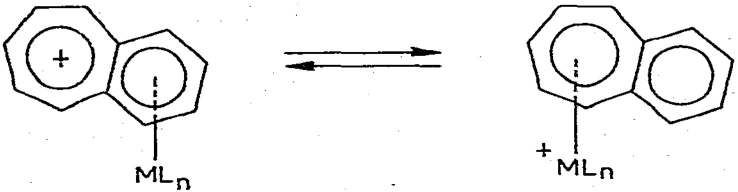
* A similar scheme may be drawn for indenyl derivatives.

Processes of this type may possibly occur in heterocyclic anions such as X, XI and in some π-isoelectronic cationic systems such as XII and XIII.



(X) (XI)



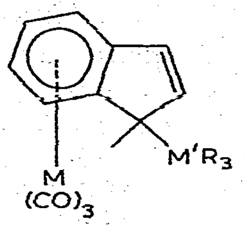
(XII) (XIII)

With neutral isomeric compounds III and IV reversible interconversions are possible if migration of the ML_n group between the five- and six-membered rings is accompanied by concerted transfer of the R group between M and the cyclopentadienyl nucleus (Scheme 1, e and f). With cyclopentadienyl-transition metal derivatives, only irreversible rearrangements with migration of an alkyl or aryl ligand from the metal atom to the cyclopentadienyl ring have been reported thus far. These lead either to formation of substituted η^4-cyclopentadiene compounds or to replacement of hydrogen in the ring. The former process occurs in reactions of $(\eta^5\text{-}C_5H_5)_2Mo(Cl)C_2H_5$ with alkylphosphines [11] and of $(\eta^5\text{-}C_5H_5)_2$-$V(CO)C_6H_5$ with carbon monoxide [12]. Replacement of a cyclopentadienyl hydrogen followed by the formation of dimeric complexes with metal—metal bonds has been reported for $(\eta^5\text{-}C_5H_5)(CO)_3MoC_2H_5$ [13], $(\eta^5\text{-}C_5H_5)(CO)_3MoC_6H_5$ [14,15], $(\eta^5\text{-}C_5H_5)(CO)_3WC_6H_5$ [14], $(\eta^5\text{-}C_5H_5)(CO)_3MoCH_2C_6H_5$, $(\eta^5\text{-}C_5H_5)(CO_3)$-$WCH_2C_6H_5$ and $(\eta^5\text{-}C_5H_5)(CO)_2FeCH_2C_6H_5$ [16].

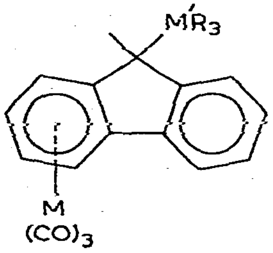
The reverse process, transfer of a substituent from the η^4-cyclopentadiene ligand to the metal atom with formation of an $(\eta^5\text{-}C_5H_5)MR$ fragment, has been observed in the reaction of $(\eta^4\text{-}endo\text{-}C_2H_5C_5H_5)(\eta^5\text{-}C_5H_5)Mo(PR_3)Cl$ with thallium borofluoride [11]. The reactions of cyclopentadiene with $(CH_3CN)_3W(CO)_3$ [17] leading to $(\eta^5\text{-}C_5H_5)(CO)_3WH$, or of $(CH_3)_3M'$—$(\eta^1\text{-}C_5H_5)$ with $(CH_3CN)_3$-$M(CO)_3$ leading to $(\eta^5\text{-}C_5H_5)(CO)_3M$—$M'(CH_3)_3$ (M = Cr, Mo, W; M' = Sn, Ge) [18] are thought to involve similar rearrangements.

The indene- and fluorene-tricarbonylmetal compounds XIV and XV appear promising objectives in the search for reversible rearrangements of types (e) and (f).

Compounds of these types are also of interest in the study of metallotropic rearrangements in η^1-cyclopentadienyl- and η^1-indenyl-non-transition metal derivatives [19,20]. Apart from the usual mechanism ([1,5]-sigmatropic rear-



(XIV)

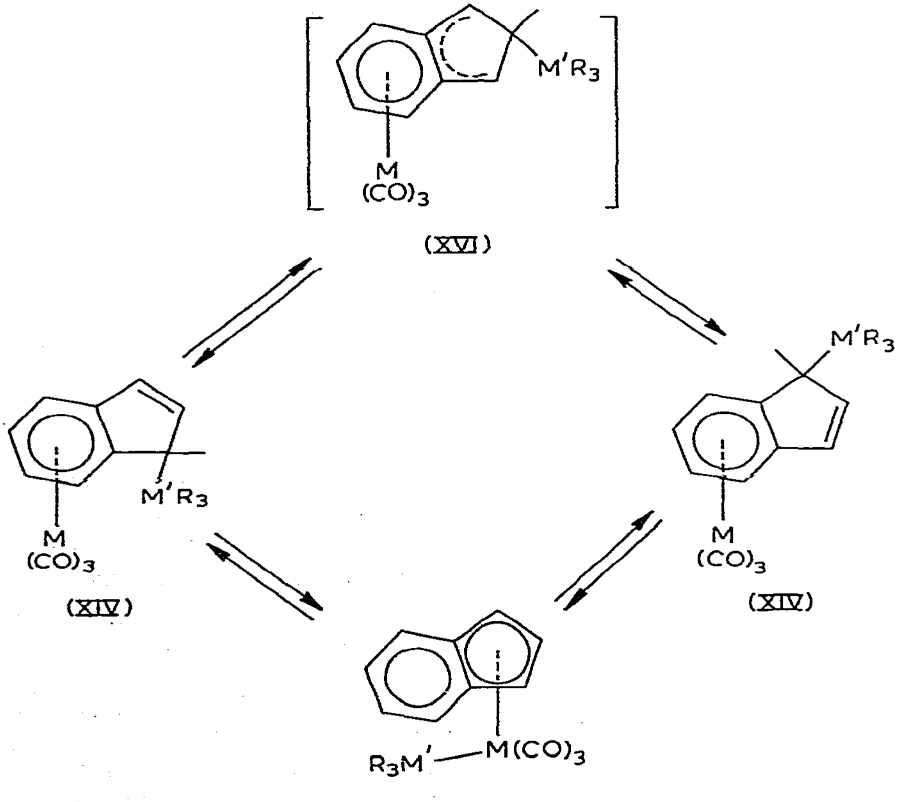


(XV)

(M = Cr, Mo, W ;
M' = Si, Ge, Sn, Pb)

rangement) with the formation of the intermediate structure XVI a "ricochet" rearrangement involving a transition metal atom is possible in this case (XVII, Scheme 2).

SCHEME 2



Lastly, there is the important and interesting problem of the reactions of anions I and II with electrophiles. Formation of both isomeric η^6- and η^5-forms III and IV (Scheme 1) is possible, even when no metallotropic equilibrium occurs between I and II because of the potentially ambident nature of these anions. Stereochemical assignment of the reaction products is of great significance for the mechanistic interpretation of reactions of anions I and II with electrophiles.

We have undertaken a detailed study of indenyl- and fluorenyl-transition metal derivatives in search of the reactions prosposed in Schemes 1 and 2. This is the first communication on the subject. It describes the synthesis of fluorenyltricarbonylchromate anion and indenyltricarbonylmetallate anions of chromium, molybdenum and tungsten, the structures of these compounds, and their reactions with certain electrophiles. The preliminary results of this investigation have been reported elsewhere [21].

Results and discussion

I. Generation of indenyl- and fluorenyl-tricarbonylmetallate anions of chromium, molybdenum, and tungsten

We have studied the following routes to indenyl- and fluorenyl-tricarbonylmetallate anions of the chromium group metals *.

(i) Interaction of indenylpotassium with $M(CO)_6$ (M = Cr, Mo, W)

$$C_9H_7K + M(CO)_6 \rightarrow \eta^5\text{-}C_9H_7(CO)_3M^-K^+ + 3\ CO \qquad (1)$$

(ii) Reduction of η^5-indenyl and fluorenyl derivatives containing metal — metal bonds:

$$[\eta^5\text{-}C_9H_7(CO)_3M]_2 + K/Na \rightarrow 2\eta^5\text{-}C_9H_7(CO)_3M^-K^+ \qquad (2)$$

$$[\eta^5\text{-}C_9H_7(CO)_3M]_2Hg + K/Na \rightarrow 2\eta^5\text{-}C_9H_7(CO)_3M^-K^+ \qquad (3)$$

(iii) Deprotonation of η^6-fluorene and indene tricarbonylmetals:

$$\eta^6\text{-}C_{13}H_{10}(CO)_3M + t\text{-}BuOK \rightarrow \eta^5\text{-}C_{13}H_9(CO)_3M^-K^+ + t\text{-}BuOH \qquad (4)$$

Routes (i) and (ii) are well known in the chemistry of the corresponding η^5-cyclopentadienyl derivatives [22]; route (iii) has been suggested for η^6-$C_{13}H_{10}Cr(CO)_3$ [1].

The advantages of method (i) are availability of starting materials and considerable yields from each run: its drawback is low purity of the anions produced. For that reason, method (i) is generally used to prepare mercury derivatives to serve as starting materials in method (ii). Methods (ii) and (iii) give high yields of anions which require no further purification before use. The choice of method of synthesis thus mainly depends on the availability of starting materials in equations 2—4.

The most suitable initial compounds for the synthesis of η^5-$C_9H_7(CO)_3Cr^-\ K^+$ (XVIII) and η^5-$C_{13}H_9(CO)_3Cr^-\ K^+$ (XIX) are η^6-$C_9H_8Cr(CO)_3$ (XX) and η^6-$C_{13}H_{10}$-$Cr(CO)_3$ (XXI), respectively. Fischer and Kriebitzsch [23] have prepared XX and XXI from $Cr(CO)_6$ and indene or fluorene by refluxing in dibutyl ether with yields of 6—7%. We have found that the reaction in diglyme at 140°C gives yields of XX and XXI of 9 and 22%, respectively. A more convenient route to both compounds is by treatment of $(NH_3)_3Cr(CO)_3$ with indene or fluorene in

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* Throughout the paper C_9H_7 stands for indenyl, C_9H_8 for indene, $C_{13}H_9$ for fluorenyl, and $C_{13}H_{10}$ for fluorene.

dioxane at 100° C, giving yields of XX and XXI of 15 and 25% respectively. This method has been suggested by Rausch and coworkers for the preparation of (η^6-styrene)Cr(CO)$_3$ [24]. Both compounds are fairly stable in the solid state, easy to purify, and readily afford anions XVIII and XIX on deprotonation (eq. 4).

The methods for preparing XX and XXI can not be used for the synthesis of η^6-$C_9H_8M(CO)_3$ (XXII, M = Mo; XXIII, M = W) and η^6-$C_{13}H_{10}M(CO)_3$ (XXIV, M = Mo; XXV, M = W). We have succeeded in preparing XXIV in yields up to 12% using the method suggested by Öfele [25] for producing arenetricarbonylchromium derivatives and modified in this laboratory [26] for syntheses of arenetricarbonylmolybdenum compounds:

$$Py_3Mo(CO)_3 + 3\ (C_2H_5)_2 \cdot BF_3 + C_{13}H_{10} \rightarrow \eta^6\text{-}C_{13}H_{10}Mo(CO)_3 + 3\ Py \cdot BF_3 \qquad (5)$$

where Py = pyridine. This method, however, fails with XXII, XXIII, and XXV. Fluorene reacts with W(CO)$_6$ in diglyme at 140° C to give XXV in only 1% yield *. In view of this we used method (ii), eq. 2 for preparing η^5-$C_9H_7(CO)_3Mo^-$ K^+ (XXVI). The dimer [η^5-$C_9H_7(CO)_3Mo]_2$ (XXVII) was made according to King and Bisnette [10], from indene and Mo(CO)$_6$ in diglyme/octane at 165° C. The use of this solvent instead of the originally suggested ethylcyclohexane [10] increased the yields to 40% and shortened the reaction time.

The dimer [η^5-$C_9H_7(CO)_3W]_2$ (XXVIII) has not been described until now. We have found that W(CO)$_6$ reacts with indene in diglyme at 175° C to give XXVIII and (η^5-C_9H_7)(η^3-C_9H_7)W(CO)$_2$ (XXIX) in yields of 1.5 and 1%, respectively **. Low availability of compound XXVIII makes it inconvenient as a starting material for the preparation of η^5-$C_9H_7(CO)_3W^-$ K^+ (XXX). For that reason, method (ii), eq. 3 was chosen for this purpose. The initial [η^5-$C_9H_7(CO)_3W]_2Hg$ (XXXI) was obtained from Hg(CN)$_2$ and η^5-$C_9H_7(CO)_3W^-$ K^+ prepared according to eq. 1.

To sum up, the preparative methods discussed above (eq. 2—4) make the anions XVIII, XIX, XXVI, and XXX available for further investigation.

II. Structures and reactions of anions XVIII, XIX, XXVI and XXX

The structure type of an indene or fluorene complex can be easily inferred from its IR and proton NMR spectra. The benzene ring proton signals shift by 1.5—2 ppm (sometimes more) upfield on π-coordination to a transition metal and appear at δ 4—5.5 ppm in the complexes. This is a general effect with all arene complexes and can therefore serve as diagnostic tool for η^6-structure assignment [27—29]. η^5-Complexes show arene proton signals only in the usual region of δ 6—8 ppm. The η^5-indenyl compounds are easy to identify by the upfield shifts of the five-membered ring proton signals giving A_2X or A_2B type patterns, and also by the characteristic AA′BB′ multiplets of the benzene protons.

Structure applications of the IR spectra are based on comparison of the spectrum of the indene- or fluorene-tricarbonylmetal derivative under investigation in the region of the C≡O stretches (1700 to 2100 cm^{-1}) with those of model η^5-cyclopentadienyl- or η^6-benzene-tricarbonylmetal compounds which are, as a rule, well known.

Nicholas and co-workers [1] have applied PMR to show that deprotonation of

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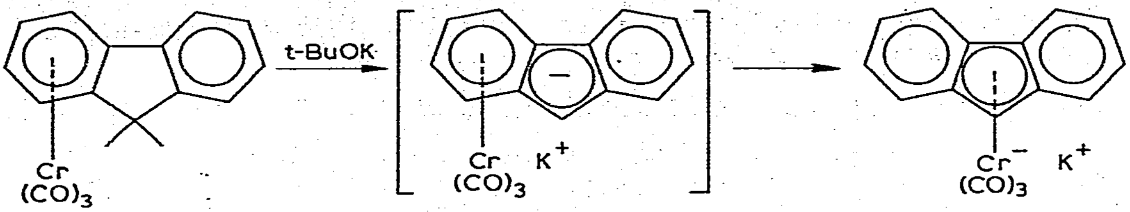
* The synthesis of compounds (XXII)-(XXV) will be described in more detail in further communications.

** The synthesis and X-ray investigation of XXIX will be reported in our next paper.

η^6-$C_{13}H_{10}Cr(CO)_3$ (XXI) leads to the anion of the η^5-series XIX. They have not however isolated the products of the reactions of XIX with $Hg(CN)_2$, CH_3I, and $(CH_3)_3SnI$. We have reinvestigated deprotonation of XXI and reactions of the anion XIX formed in solution with $Hg(CN)_2$, CH_3COOH, and CH_3I in order to determine: (i) whether the η^6 anion (XXXII) occurs as intermediate in this reaction; (ii) if it is possible to fix the η^5 structure by chemical methods; and (iii) in what way XIX reacts with electrophiles (see Scheme 1).



(XXI) (XXXII) (XIX)

The IR method provides a convenient means of following the reaction between XXI and t-BuOK. The bands of XXI at 1892 and 1966 cm^{-1} disappear while the bands of XIX at 1763, 1805, and 1904 cm^{-1} increase during the reaction *. The $\nu(C{\equiv}O)$ frequencies observed in XIX and η^5-$C_5H_5(CO)_3W^-K^+$ ** (1751, 1788 and 1895 cm^{-1}) and η^5-$C_5H_5(CO)_3Mo^-$ K^+ ** (1756, 1793 and 1900 cm^{-1}) fall close together, thus providing a convincing argument in favour of an η^5-structure for product XIX. The spectra obtained at early stages of the reaction also contain bands at 1796, 1838 and 1925 cm^{-1} absent in both XXI and XIX. The first one appears as a shoulder of the 1805 cm^{-1} band of compound XIX. The intensities of the additional bands decrease rapidly with time while the intensities of the bands assigned to XIX increase. The half-time of conversion amounts to several minutes. The C≡O stretch positions depend heavily on the effective charge on the metal atom: their frequencies shift by ca. 85 cm^{-1} on going from the neutral compound XXI to the anion XIX where chromium bears a unit negative charge. The electron density on chromium in the anion XXXII having the η^6-structure should be somewhat lower than with XIX but higher than with the neutral compound XXI. The C≡O frequencies in XXXII may therefore be expected to fall between those of XIX and XXI. It thus appears reasonable to assign the bands at 1796, 1838, and 1925 cm^{-1} to the η^6-intermediate XXXII. The problem will be considered in more detail elsewhere.

Reactions of potassium η^5-fluorenyltricarbonylchromate (XIX) with $Hg(CN)_2$, CH_3COOH, and CH_3I are shown in Scheme 3. XIX reacts with $Hg(CN)_2$ with retention of the η^5-structure. The product, bis(η^5-fluorenyltricarbonylchromium)-mercury (XXXIII) has been characterized by elemental analysis and IR spectroscopy. The IR spectrum of XXXIII in the region of the CO stretch practically coincides with those of $[\eta^5$-$C_5H_5(CO)_3M]_2Hg$ (M = Cr, Mo, W); evidently the compound has the η^5-structure. The PMR spectrum of XXXIII has not been measured because of its low solubility.

The reactions of XIX with CH_3COOH and CH_3I proceed with rearrangement

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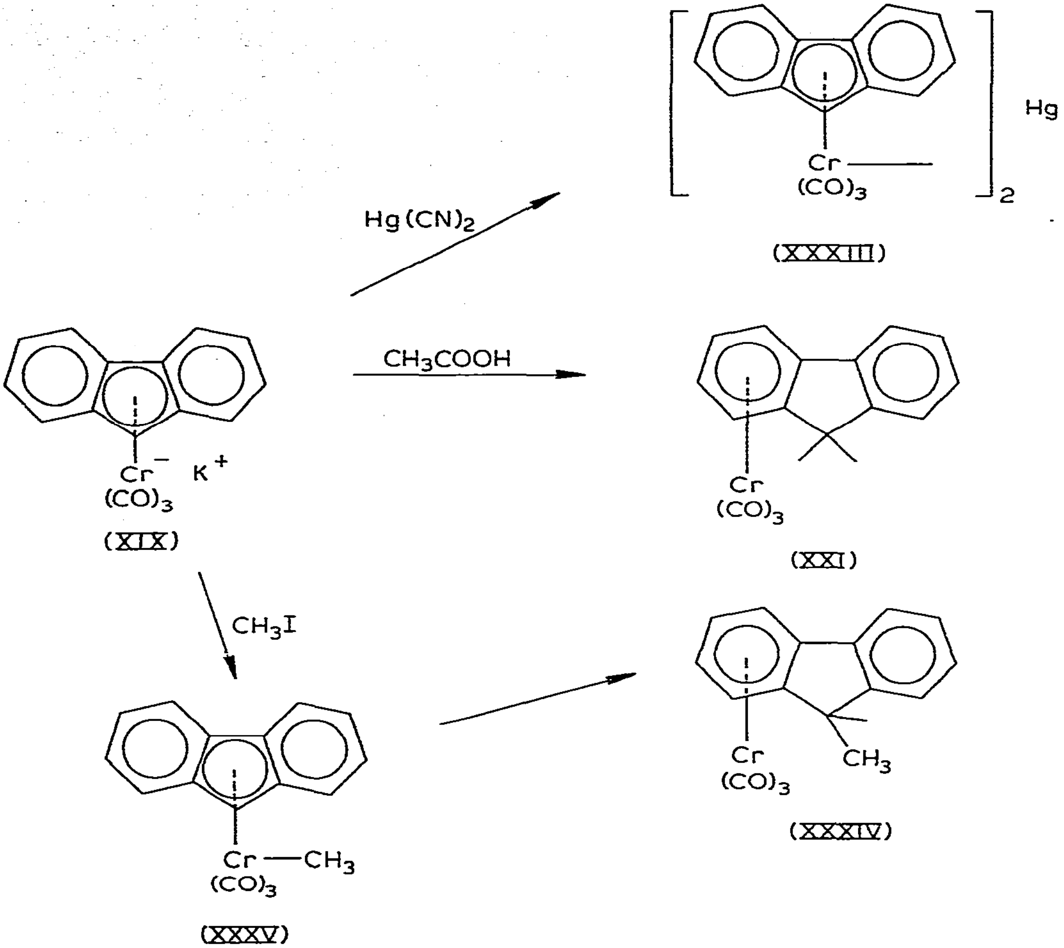
* The assignment of the 1910 and 1980 cm^{-1} bands to $\nu(C{\equiv}O)$ in XIX [1] is erroneous.

** Prepared by reduction of $[\eta^5$-$C_5H_5(CO)_3M]_2Hg$ with K/Na alloy.

SCHEME 3



to the η^6-structures XXI and XXXIV. The rearrangement is faster with CH_3COOH as evidenced by the IR spectrum, taken immediately after the addition of the acid, which only contained bands from XXI. The reaction with CH_3I proceeds via the formation of a compound giving IR bands at 1932 and 2007 cm^{-1}: at an early stage of the reaction, these are observed together with those at 1894 and 1967 cm^{-1} arising from XXXIV. The intensities of the bands at 1932 and 2007 cm^{-1} decrease rapidly with time while those of the bands from XXXIV increase. The vanishing bands have nearly the same frequencies as $\nu(C\equiv O)$ in η^5-C_5H_5-$(CO)_3CrCH_3$ [30] and may therefore be attributed to η^5-fluorenyltricarbonyl-(σ-methyl)chromium (XXXV). Conversion of XXXV to XXXIV should be a stereospecific rearrangement giving *endo*-XXXIV. The proton NMR spectrum of XXXIV in C_6D_6 seems to confirm this suggestion since only one doublet from the methyl protons is observed (δ 1.23 ppm; $^3J(H(9), CH_3)$ 7.2 Hz).

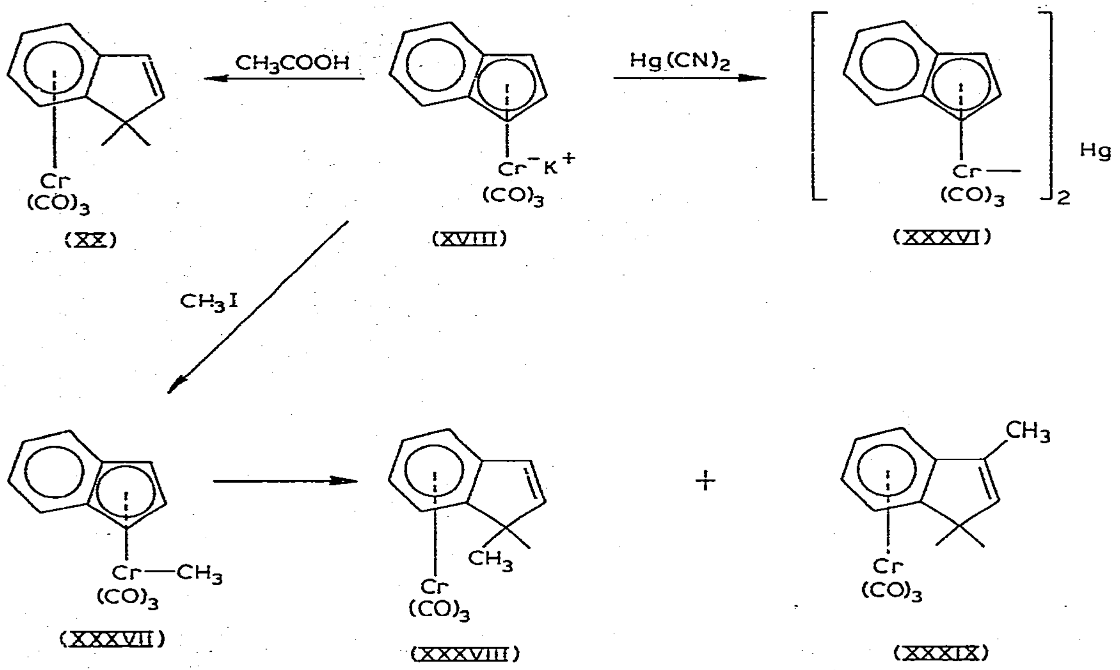
The reaction of $Cr(CO)_6$ with 9-methylfluorene carried out under the same conditions as with unsubstituted fluorene gave a mixture of the *endo*- and *exo*-isomers of XXXIV (both in low yields). Accordingly two doublets (at 0.86 and

1.23 ppm) were observed in the proton NMR spectrum of the product (^3J(H(9), CH$_3$) 7.2 Hz).

It is therefore likely that XIX reacts with CH$_3$I to give XXXIV via the σ-methyl intermediate XXXV (this pathway corresponds to processes h and f in Scheme 1). This mechanism might be proved by isolating the σ-methyl derivative XXXV.

As η^5-indenyl compounds are as a rule more stable than their fluorenyl analogues, the reactions of η^5-$C_9H_7(CO)_3Cr^- K^+$ with electrophiles might be expected to give more stable η^5-derivatives (IV, Scheme 1). In order to check this suggestion, we have studied the reactions of XVIII with Hg(CN)$_2$, CH$_3$COOH, and CH$_3$I (Scheme 4).

SCHEME 4



Anion XVIII has the η^5-structure as follows from the positions of the $\nu(C{\equiv}O)$ bands in its IR spectrum (1759, 1796 and 1899 cm^{-1}) and from the PMR spectrum (the five-membered ring protons give an A_2B pattern centred at 4.87 ppm and the benzene protons give an AA′BB′-pattern with δ_A 6.63 and δ_B 7.23 ppm (in DMSO-d_6).

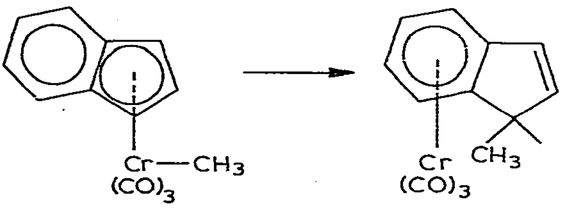
Like XIX, XVIII reacts with Hg(CN)$_2$ to give the η^5-compound XXXVI and with CH$_3$COOH to give the starting compound XX as a rearrangement product. The elemental analysis, IR and PMR spectra have been obtained for bis[(η^5-indenyl)tricarbonylchromium]mercury (XXXVI). The results point unambiguously to an η^5-structure. The IR spectrum of the product is identical to the spectrum of compound XXXIII in the region of C≡O stretch. The PMR spectrum measured in C_6D_6 contains signals from the five-membered ring protons (A_2X-pattern with δ_A 4.78, δ_X 3.98 ppm, and J_{AX} 3 Hz) and the benzene ring protons (complex multiplets at 6.64 and 7.0 ppm).

It has been already noted that XIX reacts with CH_3I to give XXXIV. On the other hand from the reaction of CH_3I with XVIII, it has proved possible to isolate and fully characterize (η^5-indenyl)tricarbonyl(σ-methyl)chromium (XXXVII), an unstable crystalline yellow-orange product rapidly decomposing at room temperature under argon even in the solid state. The PMR spectrum of XXXVII contains a δ −0.06 ppm singlet arising from the methyl group attached to chromium, signals from the coordinated five-membered ring protons (A_2X-pattern with δ_A 5.40, δ_X 4.86 ppm, and J_{AX} 3 Hz), and a 7.24 ppm signal from the aromatic ring protons. IR $\nu(C{\equiv}O)$ bands are observed at 1935 and 2010 cm^{-1}, that is at practically the same frequencies as with η^5-$C_5H_5(CO)_3$-$CrCH_3$ (1938, 2012 cm^{-1}) [30].

Even gentle (to 50° C) heating of a hexane solution of XXXVII results in its irreversible rearrangement to a two-component mixture.

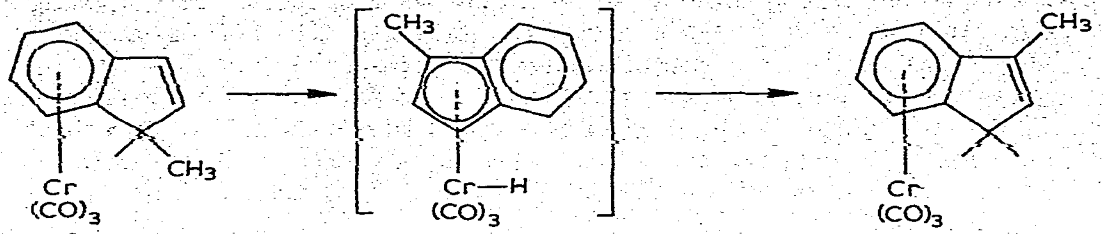
The PMR spectrum of the mixture measured in C_6D_6, reveals the presence of the η^6-isomers XXXVIII and XXXIX in a 1/2 ratio which could not be separated. The methyl group in XXXVIII is in the allyl position (doublet at 1.09 ppm, ^3J(H1), CH_3) 7.5 Hz). The two olefinic protons in this compound give a signal at 5.98 ppm, and the signal from H(1) occurs (found by double resonance experiments) at about 2.81 ppm, obscured by the CH_2 multiplet from the isomer XXXIX. The spectrum of XXXIX contains methyl and CH_2 group multiplets centred at 1.66 and 2.83 ppm, respectively, and a signal from the olefinic proton H(2) at 5.60 ppm. Irradiation of the CH_2 group signals transforms the CH_3 group signal into a doublet ($^4J(CH_3$, H(2)) 1.8 Hz): with irradiation of H(2) it becomes a triplet ($^5J(CH_3, CH_2)$ 2.0 Hz). Under irradiation of the CH_3 group signals the methylene proton signals appear as the AB part of an ABX spectrum with the X part arising from the H(2) proton (J_{AB} 23.5 Hz; ΔAB 0.39 ppm; J_{AX} 2.0, J_{BX} 2.5 Hz). The signals from the η^6-benzene proton appear at 4.23 to 5.23 ppm in both isomers and strongly overlap each other.

Intramolecular thermal rearrangement of the σ-methyl compound XXXVII may lead to the η^6-derivative XXXVIII. The results obtained in this work suggest that this is a stereospecific rearrangement: no features attributable to the isomer with the *exo*-allyl arrangement of the CH_3 group are observed, and the spectra of the *endo* and *exo* forms in C_6D_6 barely coincide in the CH_3 region. As shown above, the difference in shielding of the methyl protons in the *endo* and *exo* positions amounts to 0.37 ppm in XXXIV. With η^6-9-methylfluoreneiron cationic complexes this difference is 0.39 ppm [7].



(XXXVII) (XXXVIII)

The formation of the complex XXXIX may be regarded as either an intermolecular or an intramolecular isomerisation mechanism, the latter involving [1,5] sigmatropic rearrangement. However, the possibility of a "ricochet" rearrangement of the first-formed *exo*-methyl intermediate XXXVIII leading to XXXIX cannot be ruled out. This may proceed, e.g. according to the following mechanism.



exo-
(XXXVIII)

(XXXIX)

The results of this study will be published later in more detail.

The reactions of the salts η^5-$C_9H_7(CO)_3M^-\ K^+$ (XXVI, M = Mo; XXX, M = W) with CH_3COOH, $Hg(CN)_2$, and CH_3I have been studied under the same conditions as described for XVIII and XIX. The results are summarized in Scheme 5.

The interaction of each anion with mercury cyanide leads to the mercury derivatives of the η^5-series XL and XXXI. The structures of both compounds have been established by their PMR and IR spectra (see Table 1). The reactions with methyl iodide give the σ-methyl derivatives XLI and XLII whose PMR and IR spectra are also included in Table 1.

TABLE 1

IR AND PMR SPECTRAL PARAMETERS

Compounds		ν(C≡O) (cm^{-1}) [a]	PMR parameters [b]
			Six-membered ring
			Coordination bonded
Anions			
XVIII	η^5-$C_9H_7(CO)_3Cr^-\ K^+$	1759; 1796; 1899	
XIX	η^5-$C_{13}H_9(CO)_3Cr^-\ K^+$	1763; 1805; 1904	
XXVI	η^5-$C_9H_7(CO)_3Mo^-\ K^+$	1766; 1804; 1908	
XXX	η^5-$C_9H_7(CO)_3W^-\ K^+$	1756; 1796; 1897	
Neutral compounds of the fluorene series			
XXI	η^6-$C_{13}H_{10}Cr(CO)_3$	1892; 1966	5.19 (1H); 4.87 (1H); 4.4
XXXIV	η^6-9-CH_3-$C_{13}H_9Cr(CO)_3$	1894; 1967	4.85 (1H); 4.77 (1H); 4.2
XXXIII	$[\eta^5$-$C_{13}H_9(CO)_3Cr]_2Hg$	1890; 1957; 1983	
Neutral compounds of the indene series			
XX	η^6-$C_9H_8Cr(CO)_3$	1898; 1975	5.94 (2H); 5.01 (1H); 4.3
XXXVI	$[\eta^5$-$C_9H_7(CO)_3Cr]_2Hg$	1887; 1955; 1980	
XL	$[\eta^5$-$C_9H_7(CO)_3Mo]_2Hg$	1895; 1965; 1993	
XXXI	$[\eta^5$-$C_9H_7(CO)_3W]_2Hg$	1885; 1964; 1992	
XLIII	η^5-$C_9H_7(CO)_3WH$	1933; 2027	
XLII	η^5-$C_9H_7(CO)_3WCH_3$	1932; 1942; 2027	
XXXVII	η^5-$C_9H_7(CO)_3CrCH_3$	1936; 2010	

[a] The IR spectrum of compound XLII was measured in hexane solution: those of remaining compounds we measured in THF. [b] The proton chemical shifts are given in ppm, δ-scale (±0.01 ppm), spin coupling consta J(HH) in Hz (±0.02 Hz).

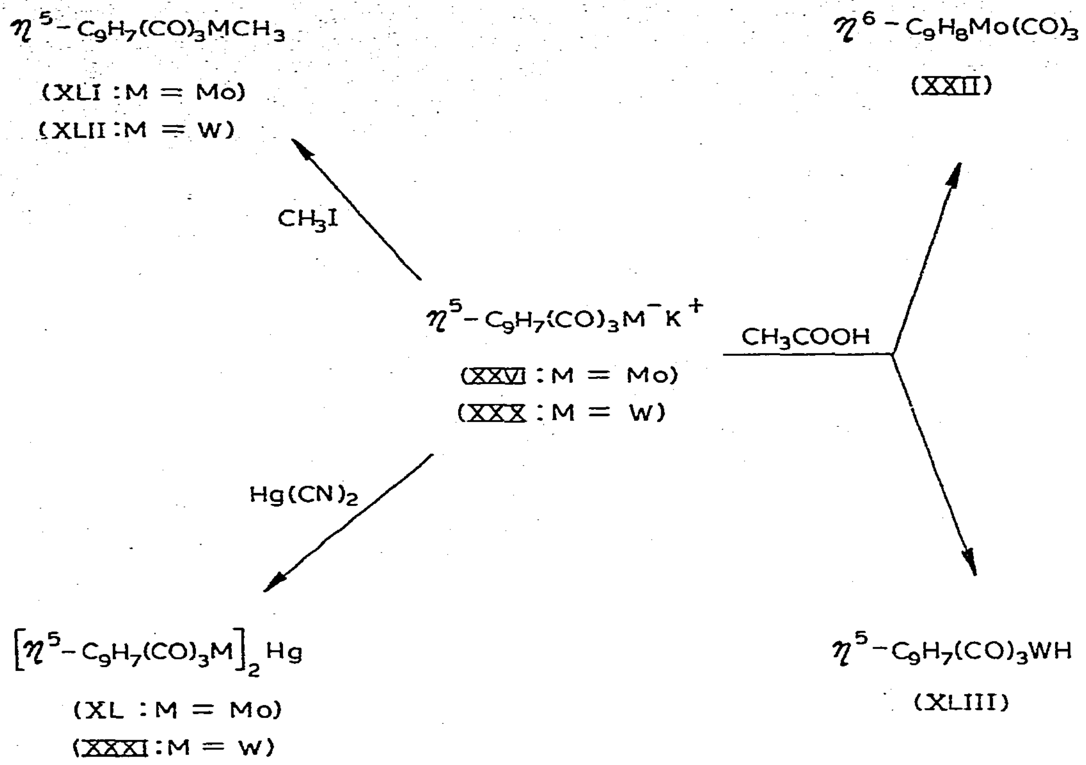
The reaction of XXVI with CH_3I has been studied earlier [10]. Protonation of XXVI and XXX proceeds by different paths. The tungsten anion XXX must react with CH_3COOH to give the stable hydride XLIII since the PMR spectrum of the product contains a high field hydride proton signal (see Table 1). The molybdate anion XXVI behaves like its chromium analogue XVIII giving a η^6-compound XXII of exceedingly low stability; only the IR spectrum could be obtained for this compound.

The results of a comparative study of the reactions of the η^5-$C_9H_7(CO)_3M^-$ K^+ (M = Cr, Mo, W) anions with electrophiles show that with chromium the η^6-structures are as a rule thermodynamically favoured over the η^5-structures, whilst stabilities of the η^5-compounds increase on going first to molybdenum and then to tungsten. (The tungsten anion XXX reacts exclusively to give η^5-derivatives.) Comparison of the relative stabilities of the η^5- and η^6-isomers III and IV (see Scheme 1) with the relative stabilities of their indenyl counterparts suggests that fluorene is more likely to form η^6-derivatives.

These conclusions are compatible with what is known about the properties of chromium group metal arene and cyclopentadienyl-tricarbonyl complexes. A more detailed study on the kinetics and stereochemistry of reactions of chromium, molybdenum, and tungsten indenyl- and fluorenyl-tricarbonylmetallate anions with a wider range of electrophiles is in progress in this laboratory.

ree	Five-membered ring	Other protons	Solvent
63; 7.23 (4H, AA'BB')	4.87 (3H, A_2B)		DMSO-d_6
2—7.8 (multiplet)	3.93 (1H, singlet)		DMSO-d_6
BCD-pattern centred at 7.00 (4H)	3.07; 3.35 (AB) J_{AB} 21.7 Hz		C_6D_6
BCD, centred at 7.21 (4H)	3.21 (1H, quartet) $J_{(H—CH_3)}$ 7.2 Hz	1.23 (CH_3, doublet)	C_6D_6
	2.61; 2.85 (AB) J_{AB} 22.0 Hz		C_6D_6
69; 7.05 (4H, AA'BB')	δ_A 4.83; δ_X 4.03 (A_2X, J_{AX} 3.0 Hz)		C_6D_6
01; 7.45 (4H, AA'BB')	δ_A 5.85; δ_X 5.33 (A_2X, J_{AX} 3.0 Hz)		$CDCl_3$
95; 7.39 (4H, AA'BB')	δ_A 5.93; δ_X 5.35 (A_2X, J_{AX} 3.0 Hz)		$CDCl_3$
17; 7.64 (4H, AA'BB')	δ_A 6.23; δ_X 5.75 (A_2X, J_{AX} 2.6 Hz)	—6.75 (1H, singlet)	$CDCl_3$
27 (4H, broad singlet)	δ_A 5.85; δ_X 5.43 (A_2X, J_{AX} 3.0 Hz)	—0.31 (CH_3, singlet)	$CDCl_3$
24 (4H, broad singlet)	δ_A 5.40; δ_X 4.86 (A_2X, J_{AX} 3.0 Hz)	—0.06 (CH_3, singlet)	C_6D_{12}

SCHEME 5



Experimental

All operations except thin layer chromatography were carried out under argon. Absolute ether solvents for use as reaction media were refluxed and redistilled under argon over K/Na alloy (THF, dimethoxyethane) or sodium metal (diglyme, dioxane) immediately before use. Alumina was of 2nd activity grade, silica gel was from Chemapol, ČSSR (L 40/100 μ).

Treatment of $Cr(CO)_6$ with fluorene

A mixture of fluorene (3.3 g, 0.02 mol) and $Cr(CO)_6$ (4.4 g, 0.02 mol) was heated to 140° C in 50 ml diglyme and 20 ml heptane for 17 h. Volatile $Cr(CO)_6$ was returned to the reaction vessel by means of a Strohmeier head [31]. The solvents and unreacted $Cr(CO)_6$ were distilled off under vacuum (0.1 mmHg) and the residue was dissolved in benzene and chromatographed on Al_2O_3 (35 × 3 cm). Unreacted fluorene was washed out with petroleum ether; the broad yellow band of η^6-fluorenetricarbonylchromium was eluted with a 1/1 benzene/petroleum ether mixture. The solvent was removed and the residue was recrystallized from benzene/heptane (benzene was distilled off under vacuum during crystallization) to give 1.31 g (22%) of compound XXI.

Reaction of $Cr(CO)_6$ with indene

Following the procedure given above, 0.55 g of η^6-indenetricarbonylchromium

(XX) (9%) was obtained from indene (3 g, 0.026 mol) and $Cr(CO)_6$ (5 g, 0.025 mol).

Treatment of $Cr(CO)_6$ with 9-methylfluorene

A mixture of 9-methylfluorene (7.33 g, 0.04 mol) and $Cr(CO)_6$ (6.28 g, 0.035 mol) in 80 ml diglyme was heated to 150°C for 8 h. Treatment of the reaction mixture following the procedure described above gave 0.2 g (2.2%) of η^6-(9-methylfluorene)tricarbonylchromium (XXXIV). The PMR spectrum was measured after the product had been recrystallized from heptane (—80°C).

Treatment of $Cr(CO)_3(NH_3)_3$ with fluorene

A mixture of fluorene (6.62 g, 0.04 mol) and $(NH_3)_3Cr(CO)_3$ (6.78 g, 0.036 mol) in 100 ml dioxane was refluxed for 4 h. After filtration, the dioxane was removed under vacuum, and the residue was dissolved in benzene and chromatographed on a column packed with alumina (3 × 40 cm). Fluorene was washed out with petroleum ether, the first broad yellow band (XXI) was eluted with benzene/petroleum ether (1/1). After removal of the solvent and recrystallization of the residue from benzene/heptane 2.73 g (25%) of XXI was obtained.

The second yellow-green band was eluted with benzene. According to IR evidence this contained $(NH_3)Cr(CO)_5$. The yield of crude product was 0.7 g (9%).

Treatment of $(NH_3)_3Cr(CO)_3$ with indene

The reaction was carried out as with fluorene to give 1.98 g (15%) of XX and 0.5 g (7%) of $(NH_3)Cr(CO)_5$ from 6 g (0.051 mol) of indene and 6.5 g (0.035 mol) of $(NH_3)_3Cr(CO)_3$.

Preparation of η^5-$C_{13}H_9(CO)_3Cr^-K^+$ (XIX)

0.14 g (0.0012 mol) of dry t-BuOK was added in one portion to a solution of XXI (0.3 g, 0.001 mol) in 50 ml tetrahydrofuran. The reaction mixture was stirred at 40—45°C for 0.5 h. Completeness of conversion was checked by IR measurements.

Preparation of η^5-$C_9H_7(CO)_3Cr^-K^+$ (XVIII)

This material was prepared as for XIX, from XX (0.3 g, 0.0012 mol) and t-BuOK (0.16 g, 0.0014 mol).

Treatment of XIX with $Hg(CN)_2$

$Hg(CN)_2$ (0.25 g, 0.001 mol) was added in one portion to a solution of XIX prepared from 0.001 mol of XXI. The mixture was stirred for an hour. After filtration, heptane was added to the solution and this was evaporated under vacuum until crystallization commenced. The orange crystals of bis[(η^5-fluorenyl)-tricarbonylchromium]mercury (XXXIII) which were obtained were then recrystallized from a benzene/heptane mixture to give 0.31 g (39%) of the product, m.p. 135°C (dec.). Found: C, 47.44; H, 2.51; Cr, 12.93; Hg, 25.84. $C_{32}H_{18}Cr_2HgO_6$ calcd.: C, 47.73; H, 2.48; Cr, 12.92; Hg, 24.92%.

Reaction of XVIII with $Hg(CN)_2$

The reaction was carried out as with XIX to give 0.24 g (29%) of bis(η^5-indenyl)-

tricarbonylchromium mercury (XXXVI) from 0.3 g (0.0012 mol) of $Hg(CN)_2$ and XVIII prepared by deprotonation of 0.0012 mol of XX. M.p. 140° C (dec.). Found: C, 41.27; H, 1.97; Hg, 28.56. $C_{24}H_{14}Cr_2HgO_6$ calcd.: C, 41.02; H, 1.99; Hg, 28.59%.

Protonation of XIX with CH_3COOH

0.0015 mol of CH_3COOH prepared by the dilution methed was added at 25° C to a solution of XIX prepared from 0.001 mol of XXI. After removal of THF under vacuum, the residue was subjected to thin layer chromatography on silica gel using 1/1 benzene/petroleum ether as eluant. Fluorene (0.05 g) and XXI (0.15 g, 50%) were isolated.

Protonation of XVIII with CH_3COOH

0.0017 mol of CH_3COOH prepared by dilution was added at 25° C to a solutio of 0.0012 mol of XVIII in THF. The solution, which had immediately turned yellow in colour, was filtered and the filtrate diluted with heptane and evaporate under vacuum to minimum volume. The precipitate which formed on cooling to —50° C was recrystallized from benzene/heptane to give 0.09 g (30%) of XX.

Reaction of XIX with methyl iodide

Methyl iodide (2 ml, 0.032 mol) was added at 25° C to a solution of XIX in THF prepared from 0.0007 mol of XXI. The mixture was stirred for an hour. After removal of THF under vacuum, the residue was extracted with benzene. The benzene solution was filtered, diluted with heptane to twice its initial volume, and evaporated under vacuum until yellow crystals of (η^6-9-methylfluorene tricarbonylchromium (XXXIV) were precipitated. The yield was 0.11 g (48%). Found: C, 64.31; H, 3.82; Cr, 16.51. $C_{13}H_{10}CrO_3$ calcd.: C, 64.56; H, 3.82; Cr, 16.5%.

Reaction of XVIII with methyl iodide

Methyl iodide (0.16 ml, 0.0025 mol) was added to a solution of XVIII prepared from XX (0.5 g, 0.002 mol). The reaction mixture was stirred at 25° C for 10 min, the solvent was then evaporated under vacuum and the residue was extracted with 2—3 portions of heptane (80 ml). The yellow solution was filtered under cooling at —80° C. The filtrate was allowed to remain at —80° C for one hour. The mother liquor was then decanted and the yellow precipitate of η^5-indenyltricarbonyl(σ-methyl)chromium (XXXVII) was recrystallized from hexane to give 0.42 g (80%) of product, m.p. 56—59° C (dec.). Found: C, 58.67; H, 4.04. $C_{13}H_{10}CrO_3$ calcd.: C, 58.65; H, 3.76%.

Thermal isomerization of XXXVII

A solution of XXXVII (0.42 g, 0.0017 mol) in 80 ml hexane was heated at 50° C for 0.5 h, then filtered and concentrated under vacuum until a yellow precipitate formed. The mixture was kept at —15° C. The mother liquor was then decanted and the crystals dried under vacuum to give 0.17 g (41%) of product, m.p. 80—82° C. Found: C, 58.94; H, 3.86; Cr, 19.22. $C_{13}H_{10}CrO_3$ calcd C, 58.65; H, 3.76; Cr, 19.55%.

Synthesis of [η^5-$C_9H_7(CO)_3Mo]_2$ (XXVII)

A mixture of $Mo(CO)_6$ (25 g), diglyme (125 ml), indene (45 ml), and octane (20 ml) was kept at 165° C for 11 h. The solvent and unreacted $Mo(CO)_6$ were then distilled off under vacuum (0.1 mmHg). The residue was dissolved in CH_2Cl_2 and the solution filtered to remove the insoluble black precipitate. After addition of hexane the solution was concentrated under vacuum to give XXVII in the form of dark violet crystals which contained small amounts of decomposition products according to TLC data. The crude material was dissolved in benzene. The solution was filtered through a fairly thin layer (3 X 10 cm) of alumina, and benzene was almost completely removed under vacuum to give 11 g (40%) of pure XXVII. The yield of XXVII based on reacted $Mo(CO)_6$ was 60%.

Preparation of η^5-$C_9H_7(CO)_3Mo^-$ K^+ (XXVI)

XXVII (0.5 g, 0.00085 mol) was added to a suspension of K/Na alloy (0.2 ml) in 30 ml THF. The mixture was stirred until the characteristic colour of XXVII disappeared (ca. 30 min). The green-yellow solution of XXVI was then filtered through a glass filter to remove excess alloy.

Synthesis of [η^5-$C_9H_7(CO)_3W]_2Hg$ (XXXI)

A solution of indenylpotassium was prepared by refluxing 6.5 ml indene with 1.5 ml K/Na alloy in 100 ml dimethoxyethane. The dark violet solution was filtered through a glass filter. 8.6 g (0.024 mol) of $W(CO)_6$ was then added and the mixture was refluxed for 2 h. After cooling the mixture to room temperature, it was treated with 9 g (0.035 mol) of $Hg(CN)_2$. The solution was stirred at 25° C for 0.5 h. Dimethoxyethane was then removed under vacuum, and the residue was extracted with 500 ml hot benzene in several portions. The benzene extract was filtered and concentrated to ca. 60 ml. The yellow crystalline precipitate of XXXI was filtered off. Further XXXI was obtained by adding methanol to the mother liquor followed by concentration and cooling of the solution to —15° C. The total yield of XXXI was 7.27 g (63%). The product decomposes at 184° C. Found: C, 29.83; H, 1.45; Hg, 20.76, W, 38.03. $C_{24}H_{14}HgO_6W_2$ calcd.: C, 29.82; H, 1.46; Hg, 20.75; W, 38.04%.

Preparation of η^5-$C_9H_7(CO)_3W^-$ K^+ (XXX)

Following the procedure given for XXVI, XXX was prepared from XXXI (0.82 g, 0.00085 mol) and K/Na alloy (0.2 ml) in 30 ml THF.

Treatment of XXVI with $Hg(CN)_2$

$Hg(CN)_2$ (0.215 g, 0.00085 mol) was added to a solution of XXVI in THF prepared from XXVII (0.5 g, 0.00085 mol). The mixture was stirred for 0.5 h. The solution was then filtered, diluted with methanol to twice its initial volume, and evaporated to small volume to give after filtration yellow crystals of [(η^5-indenyl)tricarbonylmolybdenum]mercury (XL). The yield was 0.53 g (53%). M.p. 189—191° C (dec.). Found: C, 35.77; H, 1.88. $C_{24}H_{14}HgMo_2O_6$ calcd.: C, 36.48; H, 1.78%.

Treatment of XXX with $Hg(CN)_2$

$Hg(CN)_2$ (0.215 g, 0.00085 mol) was added to a solution of XXX in THF prepared from 0.82 g (0.00085 mol) of XXXI. The solution was treated as before to yield XXXI (0.49 g, 60%).

Reaction of XXVI with methyl iodide

Methyl iodide (0.5 ml, 0.008 mol) was added to a solution of XXVI in THF prepared from 0.5 g (0.00085 mol) of XXVII. The mixture was stirred for an hour, THF was then removed under vacuum, and the residue extracted with benzene. The benzene solution was filtered through a small column of alumina (5 X 3 cm), the solvent was removed under vacuum, and the yellow crystalline residue was recrystallized from hexane to give 0.15 g (57%) of η^5-$C_9H_7(CO)_3$-$MoCH_3$. The product has been described elsewhere [10].

Reaction of XXX with methyl iodide

Methyl iodide (0.5 ml, 0.008 mol) was added to a solution of XXX prepared from 0.82 g (0.00085 mol) of XXXI. The solution was treated as before to give 0.21 (63%) of η^5-$C_9H_7(CO)_3WCH_3$ (XLII), m.p. 96°C. Found: C, 39.37; H, 2.60, W, 46.30. $C_{13}H_{10}O_3W$ calcd.: C, 39.23; H, 2.53; W, 46.19%.

Reaction of XXX with CH_3OOH

Acetic acid (0.005 mol) prepared by dilution was added to a solution of XXX in THF prepared from 0.00085 mol of XXXI. The mixture was stirred for 20 min. The solvent was then removed under vacuum, the residue extracted with 60 ml hexane, and the turbid yellow solution obtained was filtered whilst being kept at −80°C. After 2 h at that temperature the mother liquor was decanted. The yellow crystals of η^5-$C_9H_7(CO)_3WH$ (XLIII) were recrystallized from hexane. The yield of XLIII was 48% (1.6 g), m.p. 55—57°C. Found: C, 37.78; H, 2.07; W, 46.47. $C_{12}H_8O_3W$ calcd.: C, 37.53; H, 2.10; W, 47.83%.

Reaction of XXVI with CH_3COOH

Acetic acid (0.005 mol) prepared by dilution was added to a solution of XXVI in THF prepared from 0.5 g (0.00085 mol) of XXVII. The reaction was carried out at 25°C. The IR spectrum of the mixture contained weak features at 1895 and 1970 cm^{-1} indicative of the presence of XX. After the removal of THF under vacuum, the residue was extracted with benzene. According to the IR data the benzene extract contained no carbonyl derivatives.

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