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INDENYL AND FLUORENYL TRANSITION METAL COMPLEXES

III *. SOME NEW REACTIONS OF FLUORENYL- AND INDENYL-METAL TRICARBONYL ANIONS

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Summary

Deprotonation of η^6-fluorenechromium tricarbonyl (III) with excess t-BuOK in THF at —70°C yields $[\eta^6\text{-}C_{13}H_9Cr(CO)_3]^- K^+$ (Ia), which isomerizes to $\eta^5\text{-}C_{13}H_9Cr(CO)_3Cr^- K^+$ (II) at temperatures above —20°C. $[\eta^6\text{-}C_{13}H_9Cr(CO)_3]^- Li^+$ (Ib) may be obtained in the solid state by treatment of III with BuLi in absolute ether followed by precipitation with n-hexane. Methylation of Ib and II with methyl iodide goes stereospecifically to give η^6-*exo*- (IX) and η^6-(9-*endo*-methylfluorene)chromium tricarbonyl (XII) from Ib and II, respectively. Acylation of Ia with CH_3COCl yields the acetate of 9-acetylfluorenechromium tricarbonyl (VII) in its enol form. Treatment of III with excess t-BuOK and CH_3I in THF at —30°C leads to the derivative (XI), which is fully methylated at C(9). Phenyldiazonium borofluoride, diphenyliodonium iodide, ferrocenium borofluoride, trimethylchlorostannane and triethylbromogermane react with $\eta^5\text{-}C_9H_7(CO)_3M^- K^+$ in THF to give compounds of the η^5-series: $\eta^5\text{-}C_9H_7(CO)_2MN_2C_6H_5$ (M = Cr, Mo, W), $\eta^5\text{-}C_9H_7(CO)_3WC_6H_5$, $[\eta^5\text{-}C_9H_7(CO)_3M]_2$ (M = Mo, W), $\eta^5\text{-}C_9H_7(CO)_3MSnMe_3$ (M = Cr, Mo, W) and $\eta^5\text{-}C_9H_7(CO)_3MGeEt_3$ (M = Cr, Mo, W), respectively.

In the course of our studies on indene and fluorene complexes of the chromium metal carbonyls we have found deprotonation of η^6-fluorenechromium tricarbonyl (III) with t-BuOK in THF at 25°C to give

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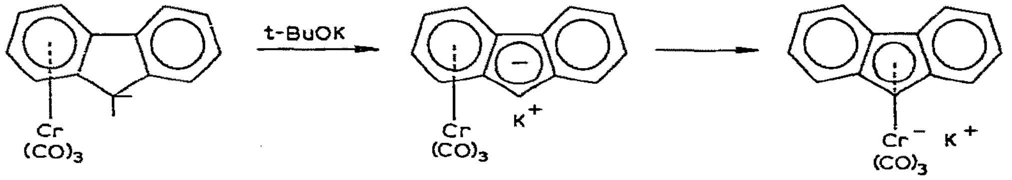
* For part II see ref. 14.

$[\eta^6\text{-}C_{13}H_9Cr(CO)_3]^- K^+$ (Ia) which isomerizes to $\eta^5\text{-}C_{13}H_9(CO)_3Cr^- K^+$ (II) [1]. The processes follow eq. 1:

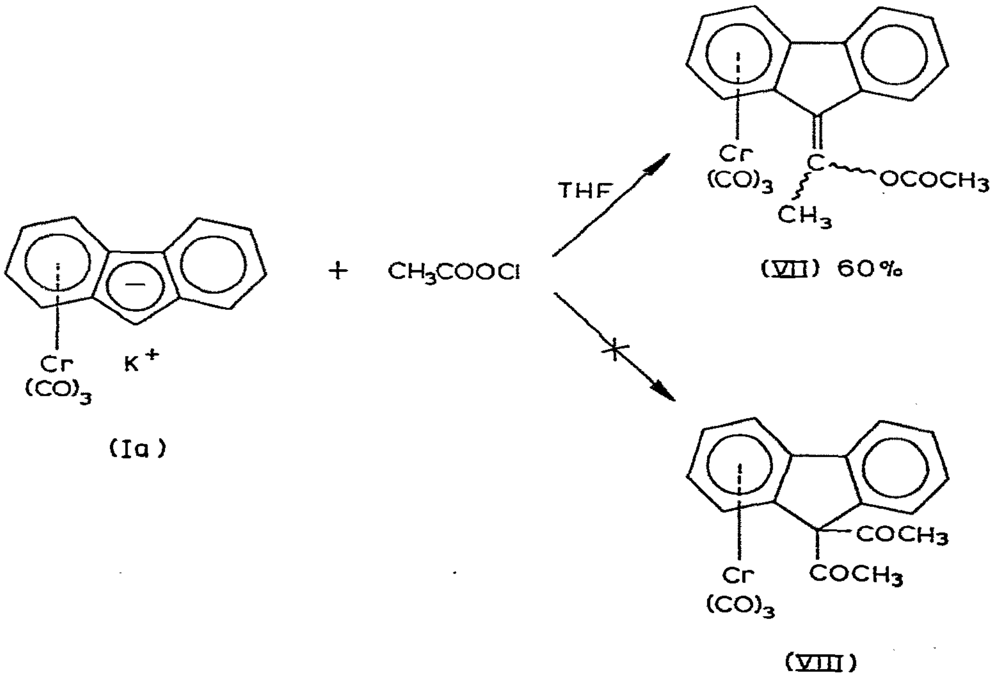


(III) (Ia) (II)

(1)

In this communication, we report on the conditions of generation of Ia in solution and corresponding the lithium salt, $[\eta^6\text{-}C_{13}H_9Cr(CO)_3]^- Li^+$ (Ib), in the solid state, the temperature limits of stability of Ia in THF solution; the stereochemistry of reactions of Ib and II with methyl iodide; and also on some novel reactions of $\eta^5\text{-}C_9H_7(CO)_3M^- K^+$ (IV, M = Cr; V, M = Mo, VI, M = W) with electrophiles.

We have found that III reacts with a threefold excess of t-BuOK in THF at −70° C, with complete conversion to Ia, as evidenced by the disappearance of its $\nu(C{\equiv}O)$ bands (1895 and 1968 cm^{-1}) and the appearance of the IR bands of Ia at 1817, 1841, and 1927 cm^{-1}. The η^6-anion Ia is stable in THF up to ca. −20° C which makes it possible to give a reliable assignment of the frequencies observed, since no other products occur in the reaction. Conversion of Ia to II manifests itself by changes in the IR spectrum at temperatures above −20° C, and does so at a sufficiently high rate at temperatures as low as 0° C. The IR bands of Ia are replaced by those of II at 1762, 1805, and 1905 cm^{-1}. The kinetics of the isomerization will be described in detail in a following communication.



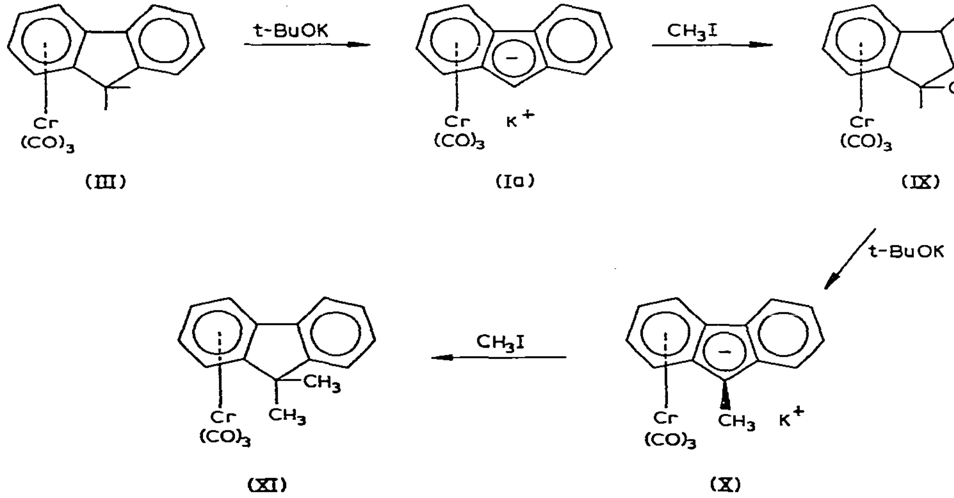
(2)

It follows from what has been said above that, in studies of reactions of Ia with electrophiles, one may take advantage of the fact that III reacts with a large excess of t-BuOK in THF at temperatures not higher than −30° C, to give Ia as practically the only product. The reaction mixture thus prepared undergoes acylation with acetyl chloride at −70° C to produce the acetate of η^6-9-acetylfluorenechromium tricarbonyl (VII) in its enol form.

In agreement with the structure suggested, the IR spectrum of VII contains bands at 1778 and 1630 cm^{-1} arising, we believe, from ester carbonyl and double bond stretches, respectively.

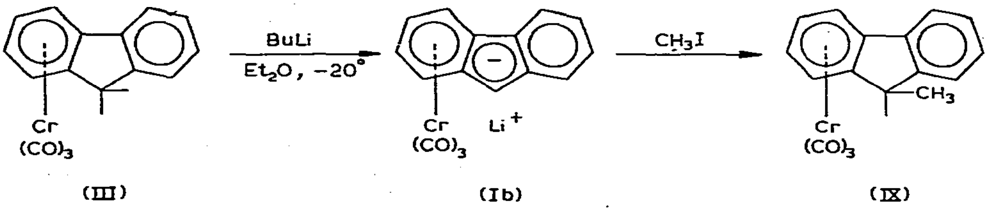
The $\nu(C{=}O)$ frequency of the isomeric compound VIII, 9,9-diacetylfluorenechromium tricarbonyl, should be not higher than 1660 cm^{-1}.

Treatment of a mixture of III and excess t-BuOK on THF with methyl iodide at −40° C, yields η^6-9,9-dimethylfluorenechromium tricarbonyl (XI), which is fully methylated at C(9) (eq. 3).



(3)

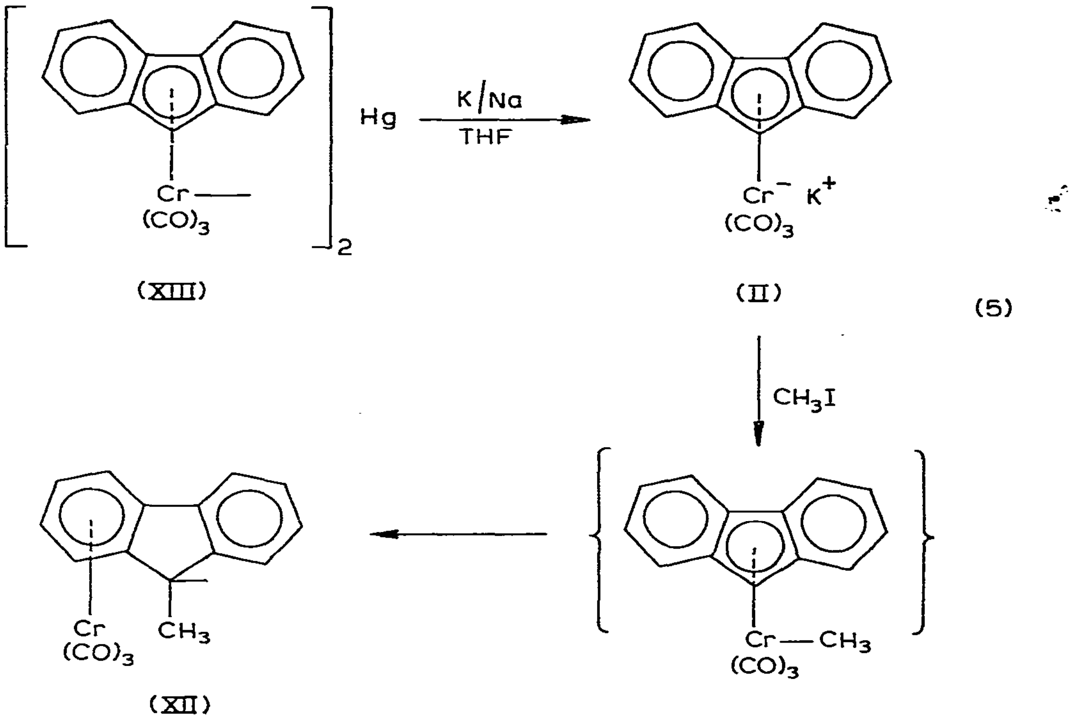
This implies that, if η^5- or η^6-anions of types Ia and II react with electrophiles to give complexes of the η^6-series containing protons at C(9), and if one is interested in the stereochemical results of these reactions, care should be taken to prevent a large excess of a deprotonating base. Otherwise secondary deprotonation can affect the reaction stereochemistry or direction. In our study on the stereochemical results of methylation of η^6-fluorenyl anion Ib, we have for this reason used an alternative route to Ib. Treatment of a saturated solution of III in ether with a solution of butyllithium in hexane at −20° C results in precipitation of Ib. To bring precipitation to completion, the solution was diluted with hexane and the solvent, together with excess butyllithium,



(4)

was removed by decantation. The precipitate was washed with cold hexane and then treated with methyl iodide in THF at —20°C. The reaction mixture was slowly warmed up to 25°C. The reaction thus conducted yields η^6-(9-*exo*-methylfluorene)chromium tricarbonyl (IX) (eq. 4).

The *exo*-isomer IX isolated from reaction 4 contains small admixtures of the starting compound III, probably because of the incomplete methylation of III with butyllithium at low temperatures and co-precipitation of III together with Ib upon the addition of hexane. The PMR spectrum of IX dissolved in benzene contains only one CH_3 doublet $\delta(CH_3)$ 1.00 ppm, $^3J(H(9), CH_3)$ 7.2 Hz. The corresponding *endo*-isomer (XII) was obtained as shown in eq. 5.



(5)

This reaction sequence has been realized by us earlier [1] where II was generated by deprotonation of III with a small excess of t-BuOK at room temperature, rather than using organomercury compound XIII. The product was purified by TLC and recrystallization. The PMR spectrum of its solution in benzene showed only one doublet for the methyl protons $\delta(CH_3)$ 1.30 ppm, $^3J(H(9), CH_3)$ 7.2 Hz *).

Our data on the difference in shielding of the *exo*- and *endo*-methyl groups in IX and XII agree with those reported by Treichel for *exo*- and *endo*-$[(9\text{-}CH_3C_{13}H_9)FeC_5H_5]^+ PF_6^-$ [2]. The methylation of Ib and II thus leads to

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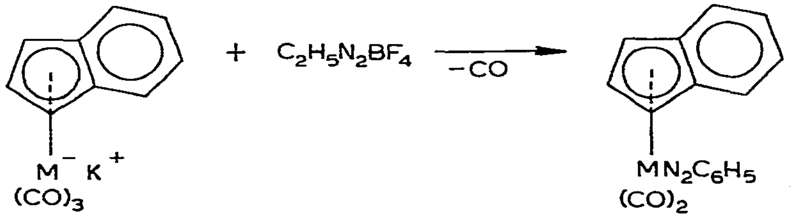
* The methyl group chemical shift values observed in solutions of IX and XII in aromatic solvents vary depending on the conditions of NMR measurements (concentration, temperature, reference compound) usually within 0.1—0.15 ppm. The relative positions of the signals, however, remain the same, the signal from *exo*-isomer IX appearing at higher fields.

different stereochemical results. It should be noted that the formation of *exo*-isomer IX from Ib is quite similar to analogous reactions of η^6-fluorenyl-iron and -manganese derivatives [2,3]. As should be expected, reaction 2 and other reactions of the η^6-anion Ia proceed more readily and require milder conditions for their completion (ca. —20 to —30°C) than does the isomerization of Ia to II.

Earlier, we have described reactions of η^5-$C_9H_7(CO)_3M^- K^+$ (IV, M = Cr; V, M = Mo; VI, M = W) with acetic acid, methyl iodide, and mercury cyanide yielding either η^5- or η^6-derivatives [1]. In the latter case, the "ricochet" mechanism may operate as shown for thermally induced isomerization of η^5-C_9H_7-$(CO)_3CrCH_3$ to mixtures of two η^6-complexes. The results obtained seem to imply that stability of the η^5-form increases on going from M = Cr to M = Mo, W. We now report on the reactions of η^5-anions IV—VI with ferrocenium and phenyldiazonium borofluorides, diphenyliodonium iodide and also with Group IV metal trialkyl halides.

The reactions were run in THF following a general procedure. An electrophile was added at – 60 to – 70°C to solutions of anions IV—VI prepared by reduction of respective organomercury compounds, $[\eta^5\text{-}C_9H_7(CO)_3M]_2Hg$, with K/Na alloy in THF. The mixtures were then allowed to warm up to room temperature while stirring. As a rule, IR spectra of mixtures thus obtained contained no bands of the initial anions. Further stirring at 25 or 40°C was only used with trialkyl-germanium and -tin halides. THF was removed under vacuum and the products were crystallized from suitable solvents.

Phenyldiazonium borofluoride readily reacts with IV—VI even at —60°C to give phenyldiazo derivatives of the η^5-series, XIV—XVI, in yields of 25 to 35%.



(6)

(IV, M = Cr;
V, M = Mo;
VI, M = W)

(XIV, M = Cr;
XV, M = Mo;
XVI, M = W)

Complexes XIV—XVI are crystalline, dark-red solids, stable in the air for a day, and readily soluble in organic solvents. IR and PMR spectra and analytical data provide an unambiguous assignment of their structures. The IR spectra of XIV—XVI in the C≡O region practically coincide with those of η^5-$C_5H_5(CO)_2$-$MN_2C_6H_5$ where M is Cr, Mo, W [4—7]. The PMR spectra contain A_2X multiplets, characteristic for the five-membered ring, and AA'BB' multiplets from benzene ring protons. Process 6 thus follows a similar scheme to that observed in analogous reactions of metal carbonyl anions of the cyclopentadienyl series [4—6].

Diphenyliodonium iodide is known to readily arylate η^5-$C_5H_5(CO)_2Fe^- Na^+$ and η^5-$C_5H_5(CO)_3M^- Na^+$ (M = Mo, W) to give the corresponding σ-phenyl derivatives [8—10]. Application of this procedure to anions IV—VI proved successful for the tungstste anion only:

$$\eta^5\text{-}C_9H_7(CO)_3W^-\ K^+ + [(C_6H_5)_2I]^+\ I^- \rightarrow \eta^5\text{-}C_9H_7(CO)_3WC_6H_5 \qquad (7)$$

(XVII) 41%

σ-Phenyl compound XVII was isolated from reaction 7 in 41% yield. Its η^5-cyclopentadienyl analogue, $\eta^5\text{-}C_5H_5(CO)_3WC_6H_5$, may be prepared similarly and in a similar yield (35—50%); the latter compound is noticeably more stable than XVII [10]. No products could be isolated from the reactions of chromate and molybdate anions IV and V with diphenyliodonium iodide. With the molybdenum anion, neither $\eta^5\text{-}C_9H_7(CO)_3MoC_6H_5$ nor its rearrangement product, were detectable in the IR spectrum of the reaction mixture, even when recorded below 0° C. Chromium anion IV gave a reaction mixture whose IR spectra contained weak features characteristic for η^6-arenechromium tricarbonyl complexes. We failed to isolate any product from this reaction because of their instability.

The reactions of η^5-anions IV—VI with ferrocenium borofluoride have been studied in order to determine the structures of radical pairing products formed in such reactions. Ferrocenium borofluoride oxidizes $\eta^5\text{-}C_5H_5(CO)_3W^-\ Na^+$ in THF at —60° C to give $[\eta^5\text{-}C_5H_5(CO)_3W]_2$ in not less than 60% yield and ferrocene in a near quantitative yield [11]. With molybdate and tungstate anions V and VI, a similar reaction yields dark-red crystalline dimers XVIII and XIX having the η^5-structure:

$$\eta^5\text{-}C_9H_7(CO)_3M^-\ K^+ + [(C_5H_5)_2Fe]BF_4 \rightarrow \{\eta^5\text{-}C_9H_7(CO)_3M^\bullet, (C_5H_5)_2Fe\} \qquad (8)$$

$$[\eta^5\text{-}C_9H_7(CO)_3M]_2 \swarrow$$

(XVIII, M = Mo, 20%;
XIX, M = W, 31%)

We assume that the reaction proceeds as one-electron oxidation of the initial anions to radicals, followed by radical pairing. It is likely that spin density in the first-formed intermediates is localised on the metal atoms. No product could be isolated from a similar reaction of chromate anion VI. After completion of this work, Birdwhistell, Hackett and Manning [12] showed that oxidation of $\eta^5\text{-}C_9H_7(CO)_3M^-\ Na^+$ (M = Mo, W) with ferric sulphate does not yield the corresponding dimers. Dimer XVIII was earlier synthesized by King [13]; its tungsten analogue XIX was obtained by thermal interaction of indene with $W(CO)_5$ in 1.5% yield [14]. Synthesis of $[\eta^5\text{-}C_9H_7(CO)_3W]_2$ according to eq. 8 has obvious advantage over that technique.

The reactions of IV—VI with trimethylchlorostannane yield η^5-compounds XX—XXII containing transition metal—tin bonds:

$$\eta^5\text{-}C_9H_7(CO)_3M^-\ K^+ + Me_3SnCl \rightarrow \eta^5\text{-}C_9H_7(CO)_3MSnMe_3 \qquad (9)$$

(XX, M = Cr, 50%;
XXI, M = Mo, 52%;
XXII, M = W, 70%)

No η^6-isomers have been observed in these reactions. Compounds XX—XXII differ significantly in their stabilities. The molybdenum and tungsten derivatives are high-melting solids; e.g. XXI may be sublimed at 90°C/0.1 mmHg without marked decomposition. The chromium derivative XX is highly sensitive to light and air, it rapidly decomposes at room temperature and has only been characterized by IR and PMR spectra.

Reactions of anions IV—VI with triethylbromogermane generally proceeded similarly:

$$\eta^5\text{-}C_9H_7(CO)_3M^- K^+ + Et_3GeBr \rightarrow \eta^5\text{-}C_9H_7(CO)_3MGeEt_3 \quad (10)$$

(XXIII, M = Cr;
XXIV, M = Mo;
XXV, M = W)

The principal difference is that the triethylgermyl derivatives XXIII—XXV are much less stable and could only be characterized by their IR and PMR spectra.

A certain amount of η^6-benzenemolybdenum tricarbonyl was isolated from the reaction of XV with Et_3GeBr, together with the bimetallic compound XXIV. This was characterized by elemental analysis, IR and PMR spectra, and by mass spectrometry. The product is thought to be formed during benzene extraction of the hexane-insoluble residue, containing compounds in which the $Mo(CO)_3$ grouping is present.

In all the reactions of η^5-anions IV—VI with $C_6H_5N_2BF_4$, $[(C_6H_5)_2I]^+ I^-$, ferrocenium borofluoride, trimethylchlorostannane, and triethylbromogermane, η^5-compounds can be identified only in cases where the products are sufficiently stable for characterisation. The search for the $\eta^5 \rightarrow \eta^6$ isomerizations seem to be more promising with fluorenyl derivatives. It should, however, be emphasized that the results obtained cannot be considered conclusive, especially for the anion η^5-$C_9H_7(CO)_3Mo^- K^+$(V), as it has been shown that η^6-benzeneMo$(CO)_3$, η^6-indeneMo$(CO)_3$ and η^6-fluoreneMo$(CO)_3$ * decompose rapidly at 25°C on dissolution in THF, dimethoxyethane, dioxane, and dimethylformamide.

In reactions of η^5-$C_9H_7(CO)_3Mo^- K^+$ with electrophiles, the formation of η^6-complexes undergoing decomposition in THF cannot be ruled out, despite no products being isolated or spectroscopically identified. Conclusive evidence for the effect of the nature of the metal on the course of reactions of η^5-$C_9H_7(CO)_3M^-$ K^+ with electrophiles, may only be gained by carrying out these reactions in solvents, where complexes of the type areneMo$(CO)_3$ are stable.

Experimental

PMR spectra were obtained with a Varian XL-100 instrument. IR spectra were recorded on an UR-20 spectrophotometer. All the operations, except thin layer chromatography, were carried out under argon. Tetrahydrofuran and 1,2-

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* We obtained the latter two complexes by treatment of $Py_3Mo(CO)_3$ with $BF_3 \cdot OEt_2$ in the presence of the corresponding arene. The yields were ca. 18%. The reaction will be described in more detail in a further communication.

dimethoxyethane were refluxed over K/Na alloy and distilled in argon flow, prior to use. Diethyl ether was purified over sodium benzophenone ketyl and distilled before use. Brockmann II activity grade alumina and silica gel were from Chemapol, CSSR (L 100/160 μ). Melting points given were not corrected. η^6-Fluorenechromium tricarbonyl and η^6-indenechromium tricarbonyl were prepared by refluxing $(NH_3)_3Cr(CO)_3$ and indene or fluorene in dioxane for 4 h, as described in ref. 1. The yields were 50 and 54%, respectively.

Acylation of I with acetyl chloride

η^6-$C_{13}H_{10}Cr(CO)_3$ (III) (0.2 g, 0.66 mmol) in 10 ml THF was added to t-BuOK (0.74 g, 6.6 mmol) in 50 ml THF at −70° C. The reaction mixture was stirred at −30 to −40° C. After metalation was completed (10 to 15 min, monitored by IR spectra), the solution was cooled to −70° C, and acetyl chloride (0.47 ml, 6.6 mmol) was added. The mixture was stirred until the reaction was complete (ca. 5 min). THF was then removed under vacuum and the residue was extracted with methylene chloride and chromatographed on silica gel in benzene/chloroform (10/1). The first yellow band contained traces of III. The second "orange-red" band was the acetate of η^6-9-acetylfluorenechromium tricarbonyl (VII) in its enol form (0.155 g, 60%). The product was recrystallized from CH_2Cl_2/heptane, m.p. 128—129° C. IR spectrum (CH_2Cl_2): $\nu(C{\equiv}O)$ 1900, 1971 cm^{-1}. PMR spectrum ($CDCl_3$) (ppm): singlets at 2.45 and 2.66 (CH_3): triplets at 5.53 and 5.32 (H_2 and H_3), doublets at 6.02 and 6.34 (H(1) and H(4)); ABCD multiplet at 7.34−7.79 (H(5)—H(8), uncoordinated ring). Found: C, 60.26; H, 3.61; Cr, 14.07. $C_{20}H_{14}O_5Cr$. calcd.: C, 60.18; H, 3.63; Cr, 13.47%.

Exhaustive methylation of III at 9 position

III (1 g, 3.3 mmol) in 10 ml THF was added to a suspension of t-BuOK (3.7 g, 33 mmol) in 50 ml THF cooled to −40° C. After stirring the mixture at − 40° C for several minutes, freshly distilled CH_3I (2ml, 33 mmol) was added to it, whereupon the solution turned from dark-red to yellow. The mixture was slowly warmed up to room temperature while stirring, THF was removed under vacuum, the residue was dissolved in benzene and the benzene solution was filtered and diluted with heptane. After removal of benzene under vacuum (water-jet pump), yellow crystals of η^6-9,9-dimethylfluorenechromium tricarbonyl precipitated. The yield was 0.98 g (90%), m.p. 88—90° C. IR spectrum (THF): $\nu(C{\equiv}O)$ 1900, 1975 cm^{-1}. PMR spectrum (C_6D_6) (ppm): singlets at 1.04 and 1.44 (CH_3); triplets at 4.34 and 4.80 (H_2, H_3); doublets at 4.98 and 5.10 (H(1), H(4)); multiplets at 6.9—7.32 (H(5)−H(8)). Found: C, 65.27; H, 4.32; Cr, 15.25. $C_{18}H_{14}O_3Cr$ calcd.: C, 65.45; H, 4.42; Cr, 15.76%.

Reaction of Ib with methyl iodide

A solution of n-butyllithium (1.1 mmol) in hexane was added to III (0.3 g, 0.99 mmol) in 45 ml ether at −20° C. The mixture was stirred at −15° C for 40 min. Ib was then precipitated by hexane addition. Hexane was removed, the precipitate was washed with more hexane and dissolved in freshly distilled THF (40 ml) cooled to −20° C. CH_3I (0.14 g, 1.0 mmol) was then added to the solution at −20° C and the mixture was stirred for 30 minutes at that temperature.

THF was removed under vacuum, the residue was treated with benzene, the benzene solution was filtered and chromatographed on silica gel in the system benzene/petroleum ether (1/1). The upper yellow band was collected and 0.17 g of yellow oil was isolated. The PMR spectrum of the product in benzene, with a solution of Me_4Si in CCl_4 as internal reference, revealed the presence of η^6-(9-*exo*-methylfluorene)chromium tricarbonyl (IX) and the starting compound III, whose percentage (10—20%) seemingly depended on the completeness of deprotonation of III. Complex IX gave a doublet at 1,0 ppm (J 7.2 Hz) (CH_3), quadruplet at 3.68 ppm (H(9)). The coordinated benzene ring signals from IX and III overlap each other (triplet at 4.66, 5.12, and 5.38 ppm).

Synthesis of $[\eta^5\text{-}C_{13}H_9(CO)_3Cr]_2Hg$ *(XIII)*

Compound XIII was synthesized as described earlier [1] with the only modification that instead of the addition of solid $Hg(CN)_2$ to a solution of II in THF, this solution was poured into an aqueous solution of $Hg(CN)_2$ as recommended for the synthesis of $[\eta^5\text{-}C_5H_5(CO)_3Cr]_2Hg$ [15]. Precipitate XIII was isolated by filtration and dissolved in methylene chloride (ca. 500 ml). The solution was then concentrated and XIII was re-precipitated by the addition of heptane. The final yield was 75%.

Reaction of $\eta^5\text{-}C_{13}H_9(CO)_3Cr^- K^+$ *(II) with* CH_3I

A solution of XIII (0.94 g) in 100 ml THF was stirred together with K/Na alloy (0.2 ml) for 30 min and then filtered through a glass filter, to remove amalgam formed and excess alloy. Excess methyl iodide (1 ml), freshly distilled over a drop of mercury in the presence of pyridine was added to the filtrate and the solution was stirred for 1 h. THF was then removed under vacuum, the residue was dissolved in benzene and chromatographed on an Al_2O_3 column. The yellow band of η^6-(9-*endo*-methylfluorene)chromium tricarbonyl (XII) was eluted first with petroleum ether and then with petroleum ether/benzene (1/1). After re-precipitation from benzene with heptane the yield of XII was 0.22 g (30%). The product was identical to that prepared earlier by methylation of II, generated by deprotonation of III with t-BuOK [1]. PMR spectrum (C_6D_6, solution of TMS in CCl_4 as internal reference) (ppm): doublet at 1.30 (J 7.2 Hz) (CH_3): triplets at 4.32, 4.82 and 5.08 (coordinated ring); quartet at 3.28 (H(9)).

Synthesis of $[\eta^5\text{-}C_9H_7(CO)_3Cr]_2Hg$ *(XXVI)*

This was synthesized as XIII from η^6-indenechromium tricarbonyl (3.64 g, 14.4 mmol), t-BuOK (2.35 g, 21.6 mmol), and $Hg(OCOCH_3)_2$ (2.3 g, 7.2 mmol). The yield was 4.14 g (81%).

Synthesis of $[\eta^5\text{-}C_9H_7(CO)_3Mo]_2Hg$ *(XXVII) and* $[\eta^5\text{-}C_9H_7(CO)_3W]_2Hg$ *(XXVIII)*

A solution of indenylpotassium was prepared by refluxing indene (6 ml, 51 mmol) with potassium metal (1.8 g, 46 mmol) in 150 ml dimethoxyethane while stirring. The dark-violet solution formed was filtered through a glass filter. $M(CO)_6$ (5.2 g $Mo(CO)_6$ or 7.0 g $W(CO)_6$, 20 mmol) was then added, the reaction mixture was stirred under reflux for 4 h, cooled to room temperature and poured into an aqueous solution of $Hg(CN)_2$ (3.04 g, 12 mmol). The precipitate formed was filtered off, dried under vacuum and extracted with several portions of hot benzene (combined volume ca. 400 ml). The benzene extract was filtered, concentrated under vacuum to ca. 50 ml, diluted to twice its volume with methanol and concentrated until crystallization began. The yellow crystalline precipitate formed upon cooling the solution to − 15°C was isolated by filtration. The yields were 5.3 g for XXVIII and 5.78 g of XXVIII (67 and 60% based on $M(CO)_6$, respectively) [1].

Synthesis of η^5-$C_9H_7(CO)_3M^-$ K^+ (IV, M = Cr; V, M = Mo; VI, M = W)

The anions η^5-$C_9H_7(CO)_3M^-$ K^+ were synthesized by reduction of the corresponding mercury derivatives XXVI—XXXVIII with K/Na alloy in THF as described earlier for $[\eta^5\text{-}C_9H_7(CO)_3W]_2Hg$ [1]. The process was monitored by following their IR spectra.

Reactions of anions IV—VI with phenyldiazonium borofluoride (general procedure)

The reagents were taken in equimolar quantities, phenyldiazonium borofluoride being added, while stirring, to cooled (−70°C) solutions of IV—VI made from XXVI—XXVIII as described above. The reactions proceeded even at as low temperature as −70°C and were accompanied by solution darkening and evolution of CO. After the mixtures were gradually warmed up to room temperature, the solvents were removed under vacuum and the residues extracted with hexane until new portions of hexane remained colourless. The cherry coloured hexane solutions were filtered, concentrated under vacuum to 25—35 ml and cooled to −20°C. Dark-red crystals of the phenylazo complexes XIV—XVI were filtered and dried under vacuum.

η^5-$C_9H_7(CO)_2CrN_2C_6H_5$ (XIV). Dark-red crystals of XIV (0.07 g, 25%) were obtained from η^5-$C_9H_7(CO)_3Cr^-$ K^+, prepared by reduction of XXVI (0.3 g, 0.4 mmol) and $C_6H_5N_2BF_4$ (0.15 g, 0.8 mmol), m.p. 74—75°C. IR spectrum (Hexane: $\nu(C{\equiv}O)$ 1917, 1983 cm^{-1}. PMR spectrum, (C_6D_6) (ppm) A_2X spectrum, δ_A 5.1, δ_X 4.49, J_{AX} 3 Hz (five-membered ring): multiplet at 6.4—7.2 ppm (six-membered ring). Found: C, 62.80; H, 4.02; N, 3.19; Cr, 15.36. $C_{17}H_{12}N_2O_2Cr$ calcd.: C, 62.19; H, 3.66; N, 3.54; Cr, 15.85%.

η^5-$C_9H_7(CO)_2MoN_2C_6H_5$ (XV). XV was obtained as dark-red crystals (0.10 g) from η^5-$C_9H_7(CO)_3Mo^-$ K^+, prepared by reduction of XXVII (0.67 g, 0.85 mmol) and $C_6H_5N_2BF_4$ (0.33 g, 1.7 mmol), m.p. 92—93°C. IR spectrum ($CHCl_3$): $\nu(C{\equiv}O)$ 1915, 1992 cm^{-1}. PMR spectrum (C_6D_6) (ppm): A_2X spectrum, δ_A 5.56, δ_X 4.9, J_{AX} 3 Hz (five-membered ring): multiplet at 6.3—7.2 (six-membered ring). Found: C, 54.76; H, 3.29; N, 7.76; Mo, 25.92. $C_{17}H_{12}N_2O_2M$ calcd.: C, 54.85; H, 3.25; N, 7.52; Mo, 26.77%.

η^5-$C_9H_7(CO)_3WN_2C_6H_5$ (XVI). η^5-$C_9H_7(CO)_3W^-$ K^+ prepared by reduction of XXVIII (0.82 g, 0.85 mmol) was treated with $C_6H_5N_2BF_4$ (0.33 g) to give XVI (0.27 g, 35%), m.p. 110—112°C. IR spectrum (hexane): $\nu(C{\equiv}O)$ 1912, 1983 cm^{-1}. PMR spectrum ($CDCl_3$) (ppm): A_2X spectrum, δ_A 6.43, δ_X 5.72, J_{AX} 3 Hz (five-membered ring); multiplet at 6.8—7.48 (six-membered ring). Found: C, 44.65; H, 2.64; N, 5.97; W, 39.86. $C_{17}H_{12}O_2W$ calcd.: C, 44.37; H, 2.63; N, 6.08; W, 39.95%.

Reaction of η^5-$C_9H_7(CO)_3W^-$ K^+ with $[(C_6H_5)_2I]^+$ I^-

Diphenyliodonium iodide (0.84 g, 2.06 mmol) was added while stirring to a cooled (—70°C) solution of η^5-anion VI, prepared by reduction of XXVIII (1 g, 1.03 mmol). The mixture was slowly warmed up to room temperature. To bring the reaction to completion, the mixture was heated at 40—45° C on a water bath until IR bands of VI completely vanished (1—2 h). THF was then removed under vacuum and the residue was crystallized from hexane to yield η^5-$C_9H_7(CO)_3WC_6H_5$ (XVII) as yellow crystals (0.40 g, 41%), m.p. 105—110° C. Analytically pure XVII may be obtained by repeated crystallization from hexane or by chromatographing on a column packed with silica gel. IR spectrum (CH_2Cl_2): $\nu(C{\equiv}O)$ 1935, 2025 cm^{-1}. PMR spectrum ($CDCl_3$) (ppm): A_2X spectrum, δ_A 5.88, δ_X 5.68, J_{AX} 3 Hz (five-membered ring), multiplet at 6.9—7.6 ppm) six-membered ring). Found: C, 47.03; H, 2.65; W, 39.33; $C_{18}H_{12}O_3W$ calcd.: C, 46.98; H, 2.60; W, 39.97%.

With diphenyliodonium borofluoride instead of $[(C_6H_5)_2I]^+$ I^- the reaction proceeds faster, but the yield of XVII decreases.

No products could be isolated from similar reactions of η^5-anions V and VI with diphenyliodonium salts.

Reaction of η^5-$C_9H_7(CO)_3W^-$ K^+ with ferrocenium borofluoride

$[(C_5H_5)_2Fe]BF_4$ (0.46 g, 1.7 mmol) was added while stirring to a cooled (—78° C) solution of VI, prepared by reduction of XXVIII (0.82 g, 0.85 mmol). The mixture was slowly warmed up to 25° C and stirred at that temperature for an hour. The solvent was then removed under vacuum. Ferrocene was extracted with petroleum ether (20 ml), the residue dissolved in CH_2Cl_2, the solution filtered, diluted with heptane and concentrated under vacuum to remove CH_2Cl_2 and to precipitate $[\eta^5$-$C_9H_7(CO)_3W]_2$ (XIX). The yield was 0.2 g (31%). The product was identical to that described by us earlier [14].

Reaction of η^5-$C_9H_7(CO)_3Mo^-$ K^+ with ferrocenium borofluoride $[\eta^5$-$C_9H_7(CO)_3Mo]_2$ was obtained in 20% yield (0.03 g) as described above, from VI prepared by reduction of XXVII (0.2 g, 0.25 mmol) and $[(C_5H_5)_2Fe]$-BF_4 (0.14 g, 0.5 mmol). The product was identical to that described in the literature [13].

Reactions of IV—VI with trimethylchlorostannane and triethylbromogermane (general procedure)

The reagents were taken in equimolar quantities. Me_3SnCl or Et_3GeBr in THF were added to solutions of anions IV—VI in THF, prepared by reduction of XXVI—XXVIII at 25° C. The reactions were monitored by following their IR-spectra. With IV (M = Cr) and VI (M = W), the reactions with Me_3SnCl were completed in 1—2 h while stirring at 25° C. With V (M = Mo), the same reaction required heating at 40—50° C for 3 h. Reactions of IV—VI with Et_3GeBr were completed in 3 h while stirring at 25° C. THF was removed under vacuum and the residue was recrystallized from hexane at reduced temperature. All bimetallic derivatives decompose when subjected to chromatography. Triethylgermyl-chromium and -molybdenum derivatives could not be isolated in the crystalline state. The PMR spectra revealed the presence of significant amounts of $(Et_3Ge)_2O$ in these products.

η^5-$C_9H_7(CO)_3WSnMe_3$ (XXII). Anions VI, prepared by reduction of XXVIII (0.7 g, 0.69 mmol), reacted with Me_3SnCl (0.09 g, 1.4 mmol) to give XXIII (0.4 g, 53%), m.p. 105—107°C. IR spectrum (THF), $\nu(C{\equiv}O)$: 1890, 1914, 1992 cm^{-1}. PMR spectrum ($CDCl_3$, Me_4Si as external reference) (ppm): A_2X spectrum, δ_A 5.83, δ_X 5.33, J_{AX} 3 Hz (five-membered ring); symmetrical multiplets centred at δ 7.05, 7.44 (AA'BB', six-membered ring), $\delta(CH_3)$ 0.5. Found: C, 33.01; H, 2.97. $C_{15}H_{16}O_3WSn$ calcd.: C, 32.94; H, 2.95%.

η^5-$C_9H_7(CO)_3MoSnMe_3$ (XXI). Anion V, prepared by reduction of XXVII (1 g, 1.26 mmol), reacted with Me_3SnCl (0.5 g, 2.5 mmol) to give XXI (0.6 g, 52%). The product sublimed at 90°C/0.1 mmHg, m.p. 92—93°C. IR spectrum (hexane), $\nu(C{\equiv}O)$: 1910, 1937, 2008 cm^{-1}. PMR spectrum ($CDCl_3$, TMS as external reference) (ppm): A_2X spectrum, δ_A 5.75, δ_X 5.26, J_{AX} 3 Hz (five-membered ring); symmetrical multiplets centred at δ 7.06 and 7.47 (six-membered ring): $\delta(CH_3)$ 0.48. Found: C, 40.46; H, 3.71. $C_{15}H_{16}O_3MoSn$ calcd.: C, 39.26; H, 3.51%.

η^5-$C_9H_7(CO)_3CrSnMe_3$ (XX). Anion IV, prepared by reduction of XXVI (0.7 g, 1 mmol), reacted with Me_3SnCl (0.4 g, 2 mmol) to give XX (0.41 g, 50%). The product rapidly decomposes at 25°C, even under argon. IR spectrum (hexane, $\nu(C{\equiv}O)$: 1896, 1926, 1990 cm^{-1}. PMR spectrum ($CDCl_3$, TMS as external reference) (ppm): A_2X spectrum, δ_A 5.42, δ_X 4.54; J_{AX} 3 Hz (five-membered ring); symmetrical multiplets centred at δ 7.08 and 7.42 (AA'BB', six-membered ring); $\delta(CH_3)$ 0.54.

η^5-$C_9H_7(CO)_3WGeEt_3$ (XXV). This was obtained as yellow crystals from anion IV, prepared by reduction of XXVIII (0.97 g, 1 mmol) and Et_3GeBr (0.36 g, 2 mmol). The yield was 0.65 g (60%), m.p. 48—49°C. IR spectrum (hexane), $\nu(C{\equiv}O)$: 1906, 1930 and 2004 cm^{-1}. PMR spectrum ($CDCl_3$, TMS as external reference) (ppm): A_2X spectrum δ_A 5.87, δ_X 5.45, J_{AX} 3 Hz (five-membered ring): two multiplets at δ 7.05 and 7.41 (AA'BB', six-membered ring): multiplet at δ 1.0—1.45 (Et_3Ge).

η^5-$C_9H_7(CO)_3MoGeEt_3$ (XXIV). The reaction mixture obtained from η^5-$C_9H_7(CO)_3Mo^-$ K^+ (prepared by reduction of 0.8 g, 11 mmol of XVII) and Et_3GeBr (0.36 g) in 50 ml THF, was stirred at 25°C for 3 h. The solvents were then removed and the residue was extracted with hexane. The hexane fraction gave 0.36 g (ca. 40%) of unstable brown oil containing XXIV, as evidenced by its IR and PMR spectra. IR spectrum (hexane), $\nu(C{\equiv}O)$: 1911, 1936, 2006 cm^{-1}. PMR spectrum ($CDCl_3$, TMS as external reference) (ppm): A_2X spectrum, δ_A 5.78, δ_X 5.38, J_{AX} 3 Hz (five-membered ring); two multiplets at δ 7.07 and 7.52 (AA'BB', six-membered ring).

The residue, after hexane extraction, was extracted with benzene; the extract was filtered, concentrated under vacuum, and precipitated with heptane to give benzenemolybdenum carbonyl (0.13 g, 25%). IR spectrum (CH_2Cl_2), $\nu(C{\equiv}O)$: 1900, 1980 cm^{-1}; $\delta(C_6H_6)$ ($CDCl_3$) 5.57 ppm. Found: C, 42.33; H, 2.90. C_9H_6Mo calcd.: C, 41.88; H, 2.34%.

η^5-$C_9H_7(CO)_3CrGeEt_3$ (XXIII). A brown oil containing XXIII, sensitive to air and light, was obtained from anion IV (prepared by reduction of XXVI, 0.7 g, 1 mmol) and Et_3GeBr (0.36 g, 2 mmol). IR spectrum (hexane), $\nu(C{\equiv}O)$: 1907, 1933, 1994 cm^{-1}. PMR spectrum ($CDCl_3$, TMS as external reference) (ppm): A_2X spectrum, δ_A 5.36, δ_X 4.68, J_{AX} 3 Hz (five-membered ring); AA'BB' spectrum, two multiplets at δ 7.12 and 7.45 (six-membered ring).

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