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Indenyl and fluorenyl transition metal complexes

XIV *. Synthesis and reactions of chromium tricarbonyl complexes of 5,10-dihydroindeno[2,1-*a*]indene

O.I. Trifonova, R.A. Galiullin, Yu.A. Ustynyuk **
Moscow State University, Department of Chemistry, Moscow 119899 (U.S.S.R.)

N.A. Ustynyuk, P.V. Petrovsky, and D.N. Kravtsov
Institute of Organo-Element Compounds, Vavilova St., 28, Moscow, 117813 (U.S.S.R.)

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Abstract

1–4,4a,10b-η^6-5,10-dihydroindeno[2,1-*a*]indene chromium tricarbonyl (III) has been obtained by Rausch's method. Deprotonation of III by t-BuOK in THF solution, by potassium solution in HMPTA or by KH in THF at −65 °C yields an η^6-anion IV, which is irreversibly rearranged into η^5-anion V at 20 °C. Action of n-BuLi/t-BuOK mixture in THF at −65 °C results in the formation of η^6-dianion VI, which is irreversibly converted into η^5-dianion VII above 0 °C. Alkylation of IV with benzyl iodide yields 5-*exo*-benzyl(III). Reaction of V with benzyl iodide leads to the σ-benzyl derivative, which is isomerized into 5-*endo*-benzyl(III). The reaction of V with *N*-nitroso-*N*-methyltosylamide yields the η^5-nitrosodicarbonyl complex of chromium (XI).

Introduction

In the course of our studies on a new type of metallotropic tautomerism that we have found for the anions of fluorenyl Group VIA metal tricarbonyl complexes, we have shown that tautomeric equilibrium (eq. 1) is determined to a large extent by the structure of polycyclic aromatic ligand and by the structure of the ion pairs existing in solution [1–5].

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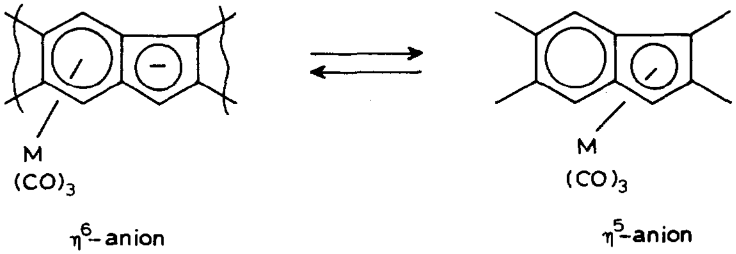
* For part XIII see ref. 10.

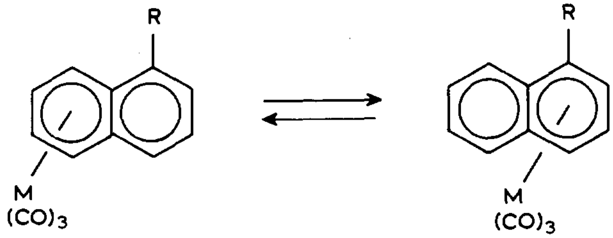
** To whom correspondence should be addressed



(1)

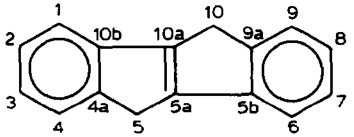
The rearrangement is possible owing to the tendency of the electron acceptor metalcarbonyl group to occupy the position with the highest electron density in the ligand.

η^6-Indenylmetaltricarbonyl anions are converted into η^5-isomers irreversibly [1,3]. When the degree of negative-charge delocalization is increased, equilibrium is shifted towards η^6-anion, and for η^6-complexes of azafluorene, benzoazafluorene and fluoradene, only η^6-anions are stable [1,3,4]. Migration of the metalcarbonyl group also occurs in neutral complexes of naphtalene [6–8]. The equilibrium (eq. 2) also depends strongly on the substituents in the ligand. Complexes, containing the donor group R ($SiMe_3$, $SnMe_3$, CH_3) are more stable, when the $Cr(CO)_3$ group is coordinated to the substituted ring.

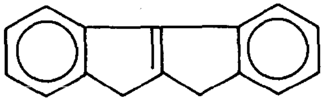


(2)

Highly interesting carbocyclic systems, which allow examination of the non-degenerate rearrangements $\eta^6 \rightleftarrows \eta^5$ and the degenerate process $\eta^5 \rightleftarrows \eta^5$, are 5,10-dihydroindene[2,1-*a*]indene (I) and 9,10-dihydroindene[1,2-*a*]indene (II), however, metalcarbonyl complexes have so far not been obtained.



(I)



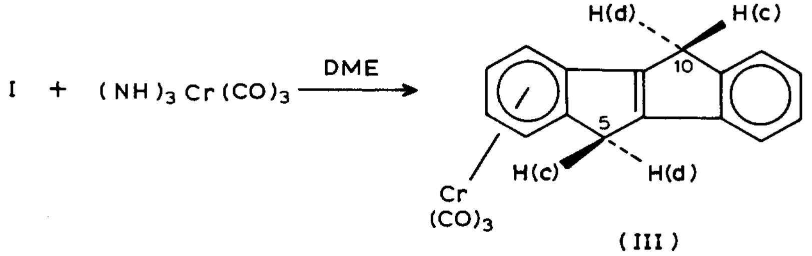
(II)

Here we describe the synthesis of 1-4,4a,10b-η^6-5,10-dihydroindene[2,1-*a*]indenechromium tricarbonyl (III), report on studies of its deprotonation and on some reactions of the anions formed.

Results and discussion

Complex III was prepared by Rausch's method by treating $(NH_3)_3Cr(CO)_3$ with I in boiling dimethoxyethane in 44% yield (based on initial I) and characterized by

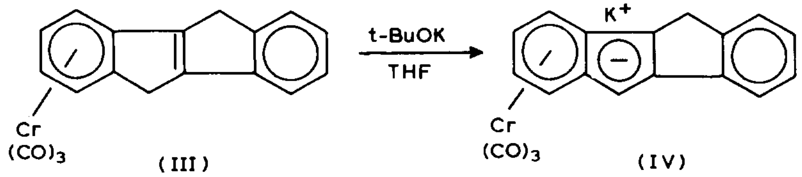
IR, NMR and mass spectroscopy, and by elemental analysis. This brownish-yellow substance is rather stable in the solid state and in solution in the absence atmospheric oxygen.



(3)

The η^6-structure of III is quite evident from the ^{1}H NMR spectrum. The signals of the coordinated benzene ring protons H(1)–H(4) are shifted upfield to 1.5–1.9 ppm from the signals of H(6)–H(9). The ABCD-spectra of the four protons at C(5) and C(10) differ markedly in $CDCl_3$ and C_6D_6 solutions. In $CDCl_3$ the chemical shifts of *exo*-H(5c) and *endo*-H(5d) coincide ($\delta = 3.75$ ppm) and the chemical shifts of two geminal protons at C(10) differ by approximately 0.15 ppm (signal with centre at 3.57 ppm). The signals in the 360 MHz spectrum are broadened owing to long range spin-spin coupling ($^5J_{H(5)H(10)}$) through 5 bonds as well as with the protons of the neighbouring aromatic nuclei. In the spectrum of III in benzene solution, signals of H(5c) and H(10c) which occupy *exo*-positions relative to the $Cr(CO)_3$ group are shifted significantly upfield owing to the ASIS-effect [10]. Chemical shifts and spin-spin coupling constants, obtained by iterative analysis by use of the program PANIC, are given in Table 1.

Deprotonation of III using an excess of t-BuOK in THF at −65 °C leads to the formation of η^6-monoanion IV, which is distinctly indicated in the ^{1}H NMR spectrum by the appearance of the H(5) singlet at 5.83 ppm. The signals of H(1,4) are revealed as a multiplet at 6.37 ppm while the signals of H(2,3), located at approximately 4.9 ppm, are obscured by the large peak of the hydroxy group proton, and the signals of the protons at C(10) in the region 3,35 ppm are partially obscured by the signal of the residual protons of THF. The IR spectrum of IV contains ν(CO) bands at 1810, 1835 (E) and 1921 cm^{-1} (A), which correspond well with IR spectrum of the η^6-fluorenylchromiumtricarbonyl anion obtained under the same conditions [2,3]. Splitting of the E-band indicates a potassium salt, IV, existing as a solvent-separated ion pair (SSIP).

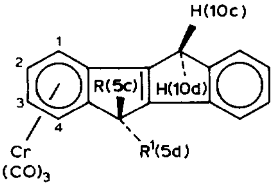


(4)

The orange coloring of a solution of IV is preserved for several hours at −60 °C, with no changes being observed in IR and ^{1}H NMR spectra. Thus no rearrangement to η^5-isomer occurs at this temperature. The same is found for the deprotonation of III by the potassium hydride in THF or by a small amount of potassium solution in HMPTA at −60 °C. In all cases deprotonation proceeds rapidly and quantitatively.

Table 1

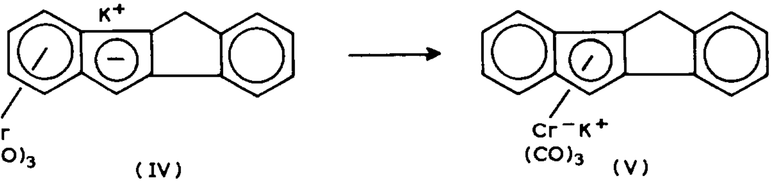
^1H NMR spectral parameters for III, VIII and X.



Substance	III (R = R^1 = H)		VIII (R = $CH_AH_BC_6H_5$, R^1 = H)		X (R = H, R^1 = $CH_AH_BC_6H_5$
Solvent	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6
Chemical shifts ($\delta \pm 0.001$ ppm)					
H(1)	5.00	5.90	5.00	5.65	4.69
H(2)	4.48	5.31	4.46	5.26	4.67
H(3)	4.48	5.31	4.39	5.16	4.07
H(4)	4.89	5.75	4.82	5.46	4.86
H(5c)	2.85	3.75			3.71
H(5d)	3.05	3.75	4.00	4.22	
H(10c)	2.84	3.57	2.88	3.53	2.85
H(10d)	3.14	3.57	3.06	3.48	3.15
H(A)			2.83	3.31	2.87
H(B)			2.72	3.03	3.28
H(6)–H(9)	7.07–7.27	7.25–7.50	6.65–7.21	6.83–7.51	
Spin-spin coupling constants (± 0.02 Hz) [a]					
J(1,2)	5.8		6.37	6.02	6.21
J(1,3)			0.94	1.08	2.02
J(1,4)			0.00	0.31	0.00
J(2,3)			6.14	5.91	5.57
J(2,4)			0.92	0.97	0.98
J(3,4)	6.7		6.22	6.27	5.88
J(5c,5d)	−21.83		–	–	–
J(10c,10d)	−22.09		−22.32	−22.46	−22.78
J(5c,10c)	3.84		–	–	3.80
J(5c,10d)	1.82		–	–	2.40
j(5d,10c)	1.99		2.05	2.37	
J(5d,10d)	3.22		3.31	2.84	
J(AB)			−13.71	−13.79	−14.09
J(5,A)			6.72	6.75	8.70
J(5,B)			7.24	7.93	7.08

[a] Iterative analysis was carried out on an Aspect-3000 computer using the program PANIC.

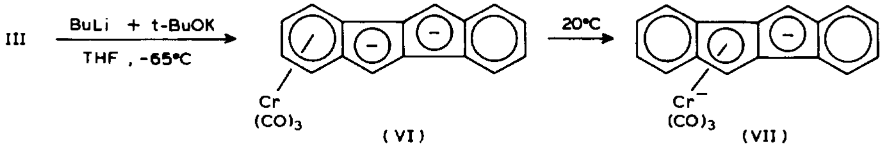
Gradual warming of the orange reaction mixture to +20 °C, causes the color of the solution to turn dark red. The intensity of the signals of IV in the ^1H NMR spectrum gradually decreases during 12–15 min and the spectrum of η^5-anion V develops: viz. a H(5)-singlet at 5.19 ppm, an AB-quadruplet of the geminal protons at C(10) centered at 3.87 ppm (*J*(AB) = 20,5 Hz), as well as complex multiplets of two different non-coordinated benzene-ring protons in the region 6.6–7.8 ppm. In the IR spectrum, ν(CO) bands at 1762, 1806 and 1902 cm^{-1} are evidence for the existence of potassium salt, V, as a contact ion pair (CIP) [2]. When dicyclohexyl-18-crown-6 is added to a solution in IR spectrum stretching vibrations collapse, and the class E and SSIP (V) bands appear at 1800 cm^{-1} and 1900 cm^{-1} respectively [2].



(5)

Thus we have established that the treatment of III with t-BuOK or KH, as well as with potassium solution in HMPTA leads to the formation of monoanions IV and V. The rearrangement from IV to V proceeds irreversibly and is much faster than that for η^6-fluorenylchromiumtricarbonyl anion, but slower than that for η^6-indenylchromiumtricarbonyl anion.

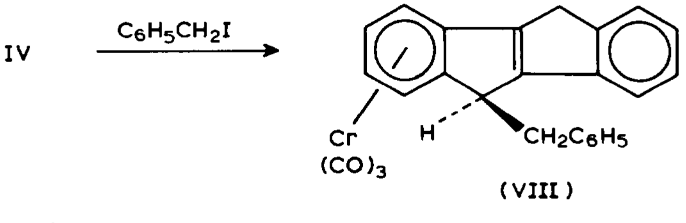
Action on III by the n-BuLi/t-BuOK mixture, which is known to be a much stronger deprotonating agent [11], leads to η^6-dianion VI in THF at −65 °C, ν(CO) bands are observed in the IR spectrum at 1810, 1835 and 1921 cm^{-1}. Two characteristic singlets (H(5) and H(10)) appear in the ^1H NMR spectrum at 5.84 ppm and 5.66 ppm, respectively. The aromatic protons give the complex patterns in the region 4.3 to 7.53 ppm, all signals being somewhat broadened. The spectrum does not undergo any appreciable changes after several hours at temperatures below −50 °C. Rearrangement of VI into η^5-dianion VII takes place when it is kept at 20 °C for 1 h.



(6)

The H(5) and H(10) singlets in the ^1H NMR spectrum of VII occur at 5.21 and 5.08 ppm. Aromatic protons give two complex multiplets one in the region 7.0 to 7.9 ppm (H(1,4), H(6,9)) and the other at 6.1–6.8 ppm (H(2,3), H(7,8)). The integral intensities ratio (1 : 1 : 4 : 4) corresponds to that expected.

We have studied the reactions of IV and V with benzyl iodide and *N*-nitroso-*N*-methyltosylamide. The reaction of η^6-anion IV with $C_6H_5CH_2I$ at −70 °C yields *exo*-5-benzyl-5,10-dihydroindeno[2,1-*a*]indenechromium tricarbonyl VIII whose structure was confirmed by ^1H NMR spectroscopy (200 MHz). Geminal protons of the CH_2-group in the benzyl fragment together with H(10c), H(10d) and H(5) protons give the ABKMX system. The spectra in $CDCl_3$ and C_6D_6 are quite different.



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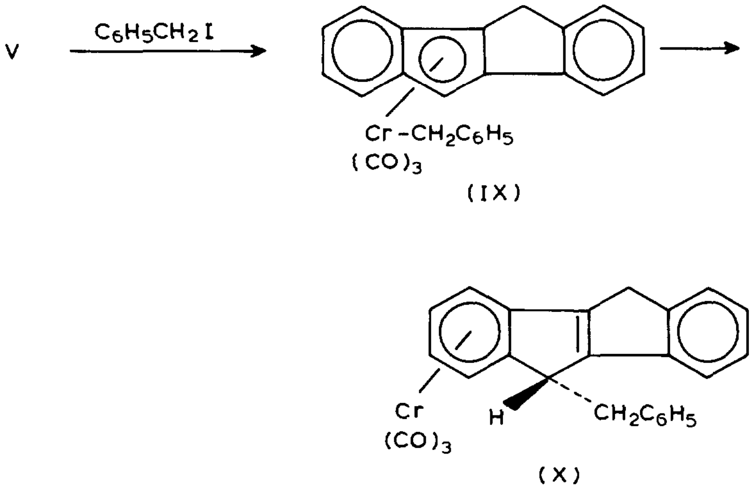
The resonance signal of H(5) occurs at 4.00 ppm in the spectrum recorded for VIII in C_6D_6 solution and at 4.23 ppm for VIII in $CDCl_3$ solution. This small ASIS



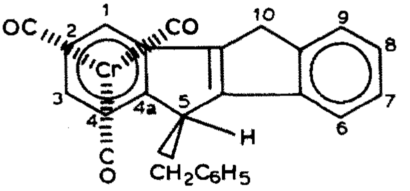
(8)

effect is characteristic for the *endo*-protons to the metal carbonyl group [10] and allows us make the following conclusion about the *endo*-orientation of H(5) in respect to the $Cr(CO)_3$ group. The ABMX patterns of the coordinated aromatic ring are well resolved in both spectra (see Table 1 for parameters). A complex multiplet of the H(6)–H(9) protons for the uncoordinated ring lies in the region 6.65–7.21 ppm for the spectrum of VIII in C_6D_6 solution and in the region 6.83–7.51 ppm for the spectrum of VIII in $CDCl_3$ solution.

The interaction of η^5-anion V with benzyl iodide was carried as follows. η^6-Anion IV was generated at −70 °C by treatment with t-BuOK in THF. The solution was warmed to +20 °C and kept at this temperature for 20 min until conversion of IV into V was complete (the reaction was monitored by IR spectroscopy). The mixture was then cooled to −30 °C and benzyl iodide added. The σ-benzyl derivative IX, the predominant product, was characterised by typical ν(CO) bands in the IR spectrum at 1938 and 2005 cm^{-1}. However, attempts to isolate IX failed owing to innersphere "ricochet" rearrangement [12] yielding *endo*-5-benzyl-5,10-dihydroindeno[2,1-*a*]indenechromium tricarbonyl (X), which was isolated by chromatography in 47% yield.

The *exo*-H(5) signal in the ^{1}H-NMR spectrum of VIII solution in C_6D_6 lies at 3.7 ppm, i.e. 0.3 ppm in higher field than the *endo*-H(5) signal in the spectrum of VIII. ASIS is about 0.5 ppm, which is characteristic for the proton in the *exo*-position relative to the $Cr(CO)_3$ group [10]. In the spectra, comparison of the patterns for the coordinated benzene rings of the isomeric *exo*-(VIII), and *endo*-(X) complexes, shows that in the *endo*-(X) complexes the difference in the chemical shifts of H(1) and H(2) had decreased significantly owing to displacement of the H(1) signal to higher field (0.3 ppm) and that of H(2) to lower field (0.2 ppm). The difference in the H(3) and H(4) chemical shifts, on the contrary, increased owing to high field displacement of the H(3) signal. This indicates the realization of the preferential conformation, Xa for the *endo*-isomer, in which anisotropic carbonyl groups localized under C(2) and C(4) carbons of the ring. The same phenomenon had been found previously for the chromiumtricarbonyl derivatives of 1-substituted indanes [13] and 9-*endo*-substituted fluorenes [10].

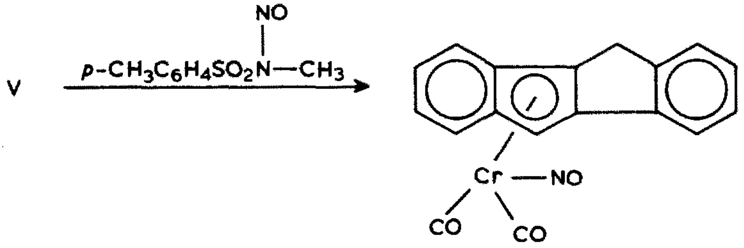
[13] and 9-*endo*-substituted fluorenes [10].



(Xa)

Large positive values for homoallylic long range spin-spin coupling ${}^5J_{(H(5)H(10))}$ in the ${}^1H$ NMR spectra of III, VIII and X indicate rigid geometry of the central structural fragment with a favorable and mutual orientation of C–H bonds. The same situation had been found previously for 1,4-cyclohexadiene [14]. Quantum chemical calculation of these coupling constants (with FP INDO approximation [15]) for the original hydrocarbon I showed both of them to be positive with ${}^5J_{cis}$ (7.2 Hz) about two times larger than ${}^5J_{trans}$ (4.7 Hz). These values calculated for I are twice as large as those observed in complexes III, VIII and X. This difference can be made smaller by optimizing the geometry of I in the calculation.

Reaction of η^5-anion V with *N*-nitroso-*N*-methyltosylamide at −30 °C readily gives nitrosyl complex XI (60% yield). This reaction proceeds in the same way as for the $C_5H_5(CO)_3Cr^-$ anion [16]. The structure of XI has been confirmed by ${}^1H$ NMR data.



(XI) (9)

From the data given above it follows that the interactions of η^6- and η^5-anions, IV and V, with benzyl iodide are regio- and stereoselective as is the case for related fluorenyl and indenyl anions. A "ricochet" rearrangement is revealed for the η^5-anion.

Experimental

All operations were carried out under pure dry argon. THF and DME were purified by boiling over K/Na alloy and distilled immediately before use. Silica gel L 100/160 (Chemapol, CSSR) was used for chromatography. Melting points are uncorrected. IR spectra were recorded on a UR-20 IR-spectrophotometer. ${}^1H$ NMR spectra were recorded on Bruker WP 200 (200 MHz), Bruker AM 360 (360 MHz) and JEOL FX-100 (100 MHz) spectrometers.

5,10-Dihydroindeno[2,1-*a*]indene (I) was obtained by cyclisation of 2,3-diphenylsuccinic acid with polyphosphoric acid [17].

η^6-5,10-Dihydroindeno[2,1-a]indenechromium tricarbonyl (III)

A mixture of 0.41 g (0.002 mol) 5,10-dihydroindeno[2,1-*a*]indene (I) and 0.37 g (0.002 mol) $(NH_3)_3Cr(CO)_3$ in 20 ml DME was boiled for 2.5 h. After filtration the solvent was removed in vacuo and the residue was chromatographed in a column on silica gel. After 0.2 g of unchanged I had been eluted with petroleum ether, III was collected in (1 : 2) benzene/petroleum ether mixture. Yield 0.16 g (44%, based on amount of I which did react), of brownish-yellow crystals. M.p. 187–190 ° C (with decomposition, in benzene/heptane). Found: C, 66.51; H, 3.97; Cr, 14.81. $C_{19}H_{12}CrO_3$ calc: C, 67.10, H, 3.56; Cr, 15.29%. ν(CO) (THF): 1893, 1967 cm^{-1}.

5-exo-benzyl-5,10-dihydroindeno[2,1-a]indenechromium tricarbonyl (VIII)

The η^6-anion IV was prepared by adding t-BuOK (0.11 g, 0.001 mol) at -70 ° C to 0.17 g (0.0005 mol) of III in 20 ml THF. The color of the solution changes from yellow to orange, with 3 bands characteristic of η^6-anion appearing in IR spectrum, viz. ν(CO) 1810, 1835 and 1921 cm^{-1}. Benzyl iodide (0.22 g, 0.001 mol) was added at the same temperature, and the solution turns yellow instantly. The mixture was then gradually warmed to room temperature, THF was removed in vacuo and the dry residue extracted with benzene. The extract was chromatographed in a column on silica gel. Yield 0.15 g (70%). M.p. 162–165 ° C (CH_2Cl/hexane). Found: C, 71.65; H, 4.51. $C_{26}H_{18}CrO_3$ calc: C, 72.55; H, 4.21%. ν(CO) (THF): 1895 and 1968 cm^{-1}.

Endo-5-benzyl-5,10-dihydroindeno[2,1-a]indenechromium tricarbonyl (X)

The η^6-anion was obtained similarly. The temperature of the reaction mixture was increased gradually during 20 min to $+20$ ° C. IR spectroscopy showed bands at ν(CO) 1762, 1806 and 1902 cm^{-1}, characteristic of η^5-anion V. The solution was dark-red. Then the reaction mixture was again cooled to -20 ° C and benzyl iodide (0.22 g, 0.001 mol) added. The IR spectrum then showed the bands ν(CO) 1938 and 2005 cm^{-1} of σ-benzyl derivative IX, which during isolation rearranges into η^6-complex X. After the solvent had been removed in vacuo, the residue was treated with benzene and the extract chromatographed in a column on silica gel; 0.1 g (47%) of X was obtained after crystallisation from CH_2Cl_2/hexane mixture as dark wine-red crystals. M.p. 170–175 ° C. ν(CO) (THF): 1895 and 1968 cm^{-1}.

Reaction of η^5-anion V with p-$CH_3C_6H_4SO_2N(CH_3)NO$

The η^5-anion (V) was prepared from 0.13 g (0.0012 mol) t-BuOK and 0.2 g (0.0006 mol) of (III). *N*-nitroso-*N*-methyltosylamide (0.24 g, 0.0012 mol) was added to the reaction mixture at -30 ° C. After the mixture had gradually attained room temperature, the THF was removed, the residue was treated with petroleum ether, and the extract chromatographed in a column on silica gel. The fraction containing XI was eluted by benzene/petroleum ether, 1 : 5, and yielded XI as dark cherry-colored crystals. Yield 0.12 g (60%). M.p. 125–126° (CH_2Cl_2/hexane). Found: C, 64.05; H, 3.55; N, 4.08. $C_{18}H_{11}CNO_3$ calc: C, 63.35; H, 3.25; N, 4.10%. ν(CO) (THF): 1960 and 2023 cm^{-1}; ν(NO) 1710 cm^{-1}. ^1H NMR (C_6D_6, 100 MHz, δ ppm): H(5) 5.48(s), H(10c), H(10d) AB pattern (J(AB) = 21,87 Hz, H(10c) 3,59; H(10d) 3,92), aromatic protons 7,36–7,9.

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