

PREPARATION OF HOMOTROPYLIUM TRANSITION METAL CARBONYL
COMPLEXES BY HYDRIDE EXTRACTION¹

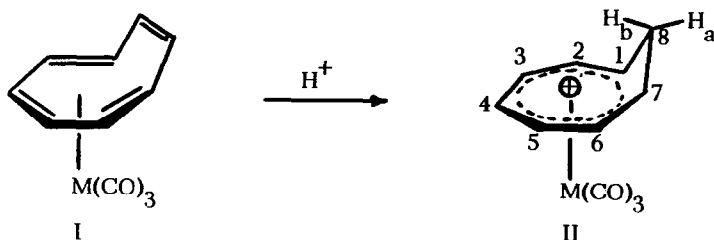
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The homoaromatic homotropylium molybdenum tricarbonyl cation³ II(M=Mo) was formerly generated in sulfuric acid solvent by protonation of the cyclooctatetraene molybdenum tricarbonyl complex I(M=Mo) prepared specifically for this purpose.^{3a} The tungsten analog of the homotropylium molybdenum tricarbonyl complex, namely II(M=W),^{3c, 4} could also be prepared in this fashion by protonation of the corresponding cyclooctatetraene complex I(M=W).^{3c, 4} These two homotropylium species were also generated by protonation and loss of CO from the corresponding cyclooctatetraene molybdenum⁵ of tungsten^{3c, 4} tetracarbonyl complexes. On the other hand, attempts to generate the homotropylium chromium tricarbonyl cation II(M=Cr) by protonation of the cyclooctatetraene chromium tricarbonyl complex⁶ I(M=Cr) were unsuccessful.⁴



We now report a convenient synthesis of homotropylium chromium, molybdenum and tungsten tricarbonyl tetrafluoroborates which permits easy isolation of the solid crystalline salts. The latter in liquid sulfur dioxide give better resolved nmr spectra than formerly obtained in H₂SO₄ solution; thus, complete analyses of the nmr spectra are possible.

The present synthesis involves hydride abstraction by the trityl cation from the 1,3,5-cyclooctatriene transition metal tricarbonyl complexes (III)⁷. The latter complexes were conveniently prepared in the present work in yields of ca.70-90% from the cyclooctatriene and (CH₃CN)₃Cr(CO)₃,^{8a} diglyme Mo(CO)₃,^{8b} or (NH₃)₃W(CO)₃,^{8c} respectively, in dioxane or THF.

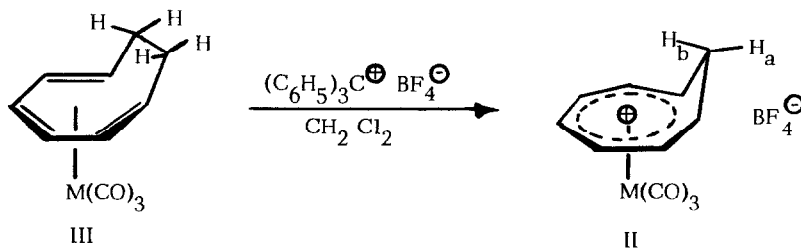
To a 600 mg. (2.48 mmole) quantity of C₈H₁₀Cr(CO)₃ dissolved in 5 ml. of CH₂Cl₂ was

added a solution of 800 mg. (2.42 mmole) of $(C_6H_5)_3C^{\oplus}BF_4^{\ominus}$ in 5 ml. of CH_2Cl_2 . A dark red microcrystalline material began to precipitate. After 20 minutes the crystals were collected, washed with 5 x 2 ml. of CH_2Cl_2 and dried in vacuo to give 605 mg. (73%) of $C_8H_9Cr(CO)_3^{\oplus}BF_4^{\ominus}$. Similarly, maroon crystals of $C_8H_9Mo(CO)_3^{\oplus}BF_4^{\ominus}$ and brown crystals of $C_8H_9W(CO)_3^{\oplus}BF_4^{\ominus}$ were obtained in 72% and 62% yields, respectively. All three homotropylium complexes are air sensitive and hygroscopic, decomposing in the presence of moisture. These salts showed no definite melting points, but decomposed gradually on heating.

Anal. Calcd. for $C_{11}H_9CrO_3BF_4$: C, 40.28; H, 2.77. Found: C, 39.63; H, 3.20.

Anal. Calcd. for $C_{11}H_9MoO_3BF_4$: C, 35.51; H, 2.44. Found: C, 35.33; H, 2.51.

Anal. Calcd. for $C_{11}H_9WO_3BF_4$: C, 28.73; H, 1.98. Found: C, 28.83; H, 2.21.



For the $Mo(CO)_3$ and $W(CO)_3$ complexes the various chemical shifts and coupling constants are obtainable directly from the spectra. For the $Cr(CO)_3$ complex, $\tau_{3,5}$ and $\tau_{2,6}$ are very similar, so the pertinent chemical shifts and coupling constants were obtained by successive approximation using the Bothner-By LAOCN3 program⁹ for a seven spin system (τ_{1-7}) to simulate the spectrum in the H_{2-6} region. All the derived chemical shifts and coupling constants are summarized in Table I.

For comparison of the nmr spectra of the complexes with that of the free ligand in SO_2 solvent, $C_8H_9^{\oplus}FSO_3^{\ominus}$ was obtained as a yellow crystalline material by reaction of equimolar amounts of cyclooctatetraene and FSO_3H in liquid SO_2 at -60° . The nmr spectrum of this salt in more dilute SO_2 solution is also summarized in Table I.

The tropylium-like electronic description of the $C_8H_9^{\oplus}$ species as the free ion and in its complexes is in accord with two general features of their nmr spectra referred to previously for the free homotropylium cation and its $Mo(CO)_3$ complex.³ One of these features is the chemical shift difference (Δ) between inside and outside H_{8b} and H_{8a} protons, respectively. According to the present data, the Δ values, summarized in Table II, are large not only for the free $C_8H_9^{\oplus}$, but also for the three complexes as well. The observed sequence of Δ values is $C_8H_9^{\oplus} > C_8H_9Cr(CO)_3^{\oplus} > C_8H_9Mo(CO)_3^{\oplus} > C_8H_9W(CO)_3^{\oplus}$. This sequence of Δ values is most simply taken as the sequence of the magnitudes of the aromatic ring current in the four species. However, Δ values are quite sensitive to molecular geometry, so until x-ray structure analysis is carried out on these species, we can't evaluate the quantitative effect of molecular geometry on the Δ values.

Table I.

Summary of NMR Spectra^a of Homotropylium Fluorosulfonate and Homotropylium M(CO)₃ Tetrafluoroborate Complexes

	C ₈ H ₉ [⊕]	C ₈ H ₉ M(CO) ₃ BF ₄ [⊖]		
		Cr	Mo	W
τ _{3,5}	1.4	3.38 ^b	3.38	3.43
τ _{2,6}	1.4	3.47 ^b	3.87	4.02
τ ₄	1.4	4.32 ^b	4.06	4.20
τ _{1,7}	3.30	5.63	5.58	5.71
τ _{8a}	4.74	6.60	6.53	6.21
τ _{8b}	10.55	11.05	10.15	9.72
J _{4,5} = J _{3,4}	- ^c	10.0 ^b	10.0	10.0
J _{5,6} = J _{2,3}	- ^c	7.5 ^b	7.5	7.5
J _{6,7} = J _{1,2}	- ^c	8.0 ^b	8.0	8-9
J _{1,8a} = J _{7,8a}	7.0	8.5	8.5	8.5
J _{1,8b} = J _{7,8b}	10.0	10.0	9.0	9.0
J _{8a,8b}	7.0	11.5	12.5	11.5

^a In ca.10% liquid SO₂ solution; internal TMS; ^b the spectrum was well simulated by means of the Bothner-By LAOCN3 program⁹ using these parameters; ^c the spectrum was not analyzed completely because of second order coupling between protons 2, 3, 4, 5 and 6.

Table II.

Some Features of the NMR Spectra of C₈H₉[⊕] and C₈H₉M(CO)₃[⊕] Species

Species	Δ	Ave. τ ₂₋₆	τ ₁₋₇ in C ₇ H ₇ [⊕] species ¹⁰
C ₈ H ₉ [⊕]	5.85	1.4	0.72
C ₈ H ₉ Cr(CO) ₃ [⊕]	4.45	3.60	3.42
C ₈ H ₉ Mo(CO) ₃ [⊕]	3.62	3.71	3.82
C ₈ H ₉ W(CO) ₃ [⊕]	3.51	3.82	3.83

The other feature of the nmr spectra of the $C_8H_9^{\oplus}$ species indicating a homotropylium electronic structure is the close comparison between average τ values for H_{2-6} in the homotropylium species and the τ_{1-7} value observed for the corresponding parent tropylium species.^{3b} As shown in Table II, the average τ_{2-6} for the free $C_8H_9^{\oplus}$ agrees with τ_{1-7} for $C_7H_7^{\oplus}$ within 0.7 ppm in liquid SO_2 solvent. The agreement is even better between τ_{2-6} for the $C_8H_9^{\oplus}$ complexes and τ_{1-7} in the corresponding $C_7H_7^{\oplus}$ complexes¹⁰ in liquid SO_2 . Thus, for the three complexes, τ_{2-6} for the $C_8H_9^{\oplus}$ species agree with τ_{1-7} for the $C_7H_7^{\oplus}$ complexes to within 0.1 ppm on the average. It is quite remarkable how closely the electronic state of carbon atoms C_{2-6} in the homotropylium species simulates that for C_{1-7} in the parent tropylium analogs.

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