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THE REACTIVITY OF COMPLEXED CARBOCYCLES

VIII *. STEREOSPECIFIC PREPARATION AND REACTIVITY OF METAL CARBONYL COMPLEXES OF BICYCLO[4.2.1]NONATRIENONE AND ITS DERIVATIVES

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Summary

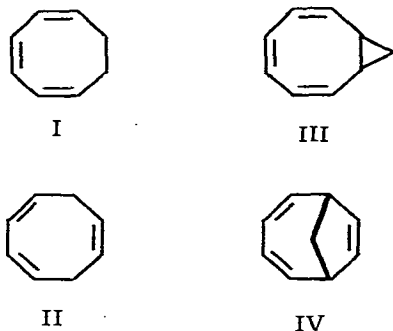
Bicyclo[4.2.1]nona-2,4,7-triene-9-one (V) reacts smoothly to form tricarbonylmetal complexes with $M = Mo, Cr, Fe$. For $M = Fe$ the *exo* and *endo* isomers could be prepared selectively by variation of the reaction conditions. While the *endo* isomer reacts with $NaBH_4$ to give the corresponding alcohol, the *exo* isomer is not reducible. Both isomers are, however, easily hydrogenated at the noncomplexed double bond. 9-Methylenebicyclo[4.2.1]nona-2,4,7-triene forms $Mo(CO)_3$ and $Cr(CO)_3$ complexes, in which the metal coordinates in an unprecedented *exo* fashion rather than in the expected *endo* mode.

^{13}C chemical shift data for the new complexes are reported which support the structural and stereochemical assignments.

Introduction

Metal carbonyl complexes of cyclic conjugated triolefins such as cycloocta-1,3,5-triene (I) have been known for a long time [1]. We recently reported that the preparation of the corresponding complexes of nonconjugated triolefins, e.g., cycloocta-1,3,6-triene (II), is also possible under mild reaction conditions [2,3]. At higher temperatures they rearrange, by metal-catalysed hydrogen migrations, to complexes of I.

* For part VII see ref. 13. This article is also part XXIII of the series ^{13}C NMR spectroscopy, for part XXII see ref. 14.



In the case of $\text{Cr}(\text{CO})_3$ and $\text{Mo}(\text{CO})_3$ complexes of bicyclic derivatives of I and II, we have shown previously that $(\text{III})\text{M}(\text{CO})_3$ rearranges at elevated temperatures to $(\text{IV})\text{M}(\text{CO})_3$ [2,4,5]. This is supported by stereo models, which suggest that the three double bonds of IV are more favourable arranged than those of III to occupy three coordination sites in octahedral complexes. In the case of iron tricarbonyl complexes of III and IV, where only two double bonds are required for coordination, the possibility of *exo-endo* isomerism exists for both III and IV. This, however, has never been observed in the well explored coordination chemistry of III and its derivatives [6], where only one product is found, while the organometallic reactivity of IV has not been much investigated because of its poor availability.

A derivative of IV is the ketone bicyclo[4.2.1]nona-2,4,7-triene-9-one (V), readily prepared from cyclooctatetraene [7], and we used this olefin as the first substrate.

By varying the nature and the bulk of the substituents at the bridge carbon C(9), we hoped to get an insight into the feasibility and restrictions of *exo* coordination to V and its derivatives. A further aim was the study of organometallic *exo-endo* isomerism by spectroscopic means, mainly ^{13}C NMR spectroscopy, and a comparison with previously investigated examples [8].

Results and discussion

To confirm the similarity of IV and V with respect to their use as complex-forming olefins, we first prepared the $\text{Mo}(\text{CO})_3$ and $\text{Cr}(\text{CO})_3$ compounds of V by standard methods (Scheme 1). They are readily isolated as red crystalline needles (Table 2), although the yield was somewhat poorer than with other triolefins.

On treatment of V with $\text{Fe}_2(\text{CO})_9$, we expected to obtain a mixture of *exo-endo* isomers of the $\text{Fe}(\text{CO})_3$ complexes, since Dreiding models of V suggest that access to the two conjugated double bonds is unhindered from both sides. When we carried out this reaction in benzene at 60°C we isolated in good yield a yellow solid with the analytical composition $\text{C}_9\text{H}_8\text{OFe}(\text{CO})_3$. To our surprise the spectroscopic data (Tables 1,2) indicated that one isomer (VIII) was formed exclusively.

Under different reaction conditions, e.g., by using n-octane as solvent at 125°C or methanol at 60°C , a mixture of two isomers was obtained. This mixture proved very difficult to separate due to the very similar properties of the

TABLE 1

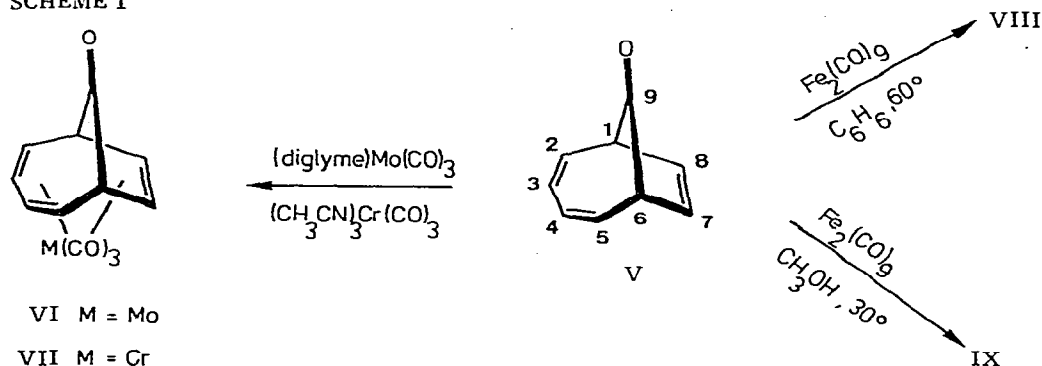
^{13}C NMR DATA FOR COMPLEXES VIII–X, XII–XIV, XVI AND XVII, IN C_6D_6 , PROTON-NOISE-DECOUPLED, CHEMICAL SHIFTS IN ppm RELATIVE TO TMS

Complex	Assignment						
	C(7, 8)	C(3, 4)	C(2, 5)	C(1, 6)	C(9)	C(10)	CO
VIII	138.7	87.2	54.5	46.7	196.5		209.5
IX	137.7	92.4	72.8	52.6	200.7		210.1
X	142.0	91.9	66.0	46.6	79.9		211.2
XII	26.8	87.1	62.4	43.5	204.9		209.9
XIII	27.0	90.1	67.4	49.1	^a		210.6
XIV	30.9	89.2	60.6	43.0	78.6		^a
XVI	136.9	90.7	59.9	43.4	48.5	65.2	223.9
XVII	136.5	91.2	59.0	41.8	40.2	68.0	^a

^a Not observed due to low intensity.

isomers. Reaction in methanol at 30°C , however, gave the second isomer (IX) in high purity (Scheme 1), thus making sophisticated separation techniques unnecessary.

SCHEME 1



The two compounds showed different absorptions in the infrared (Table 2), both typical of iron tricarbonyl compounds. The absorption of the keto group was virtually unchanged compared with that of free V, and so no distinction

TABLE 2

$\nu(\text{CO})$ DATA [cm^{-1}] FOR COMPLEXES VI–XIV, XVI AND XVII.

VI	1776	1913	1924	1995
VII	1776	1909	1919	1989
VIII	1775	1988	2007	2064
IX	1781	1992	1997	2059
X		1984	1992	2053
XI		1958	2012	2030
XII	1765	1986	2005	2063
XIII	1765	1992 ^a		2058
XIV		1984 ^a		2051
XVI		1907	1923	1996
XVII		1900	1914	1985

^a Broad adsorption.

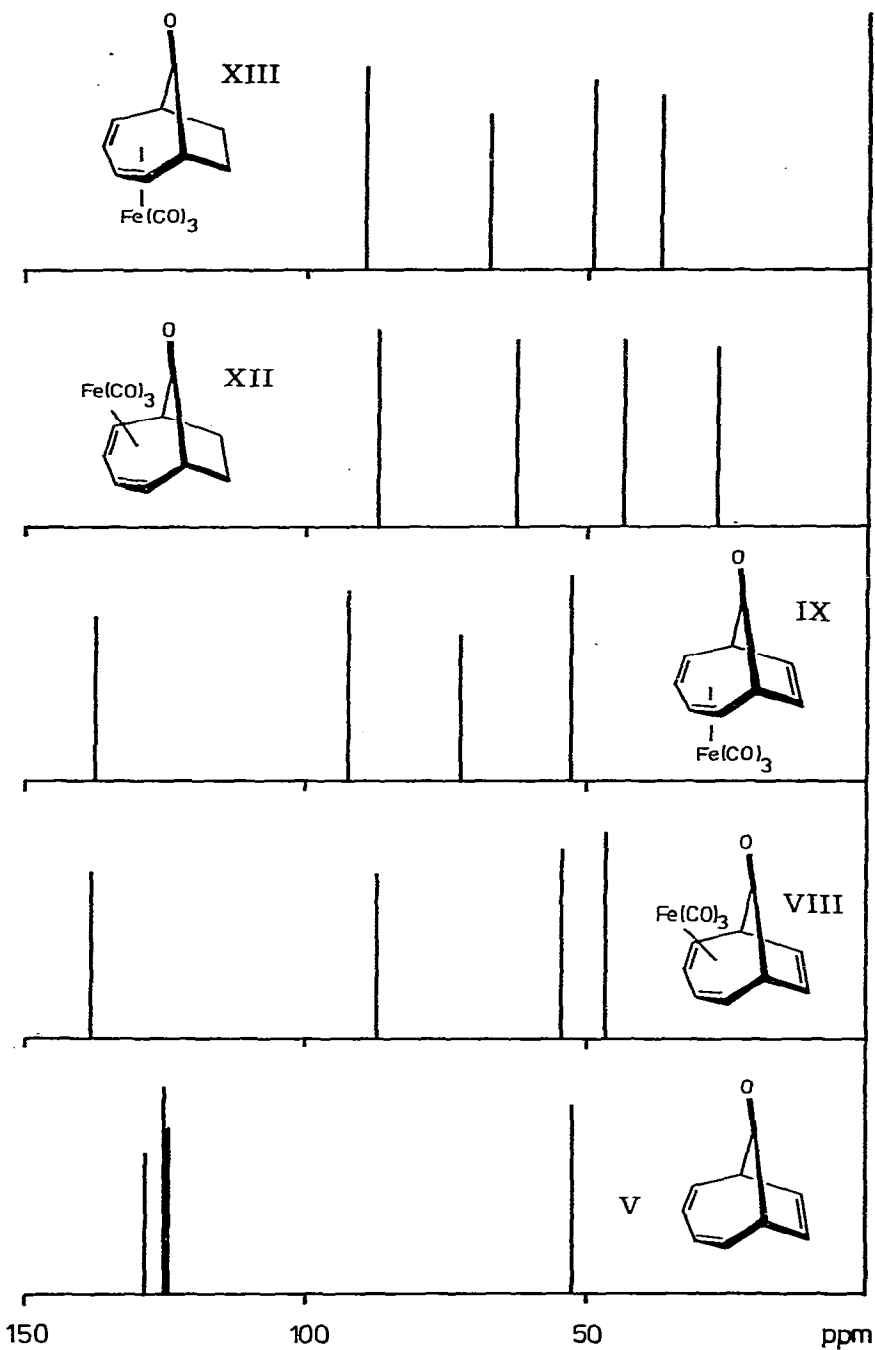
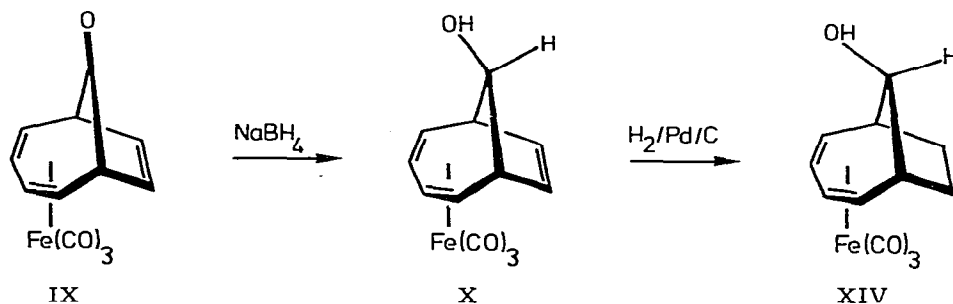


Fig. 1. ^{13}C NMR spectra of V, VIII, IX, XII, and XIII (olefinic and aliphatic region only, in C_6D_6 , proton-noise-decoupled, chemical shifts see Table 1 and Experimental).

between the *exo* and *endo* isomer could be made in that way. The ^{13}C NMR spectra showed a marked difference in the chemical shifts for VIII and IX (Table 1, Fig. 1) although again these spectra did not provide a definite assignment of *exo* or *endo* configuration. Only on comparison with previously collected data of chemical shifts for a variety of (propellane) $\text{Fe}(\text{CO})_3$ compounds, where the stereochemistry had been established by X-ray crystallography, did a definite trend emerge. A shift to higher field, especially for the coordinated olefinic carbons, is observed for the *exo* isomers compared with the *endo* compounds [8]. This suggested accordingly an *exo* configuration for VIII and an *endo* configuration for IX.

An unambiguous support for this assignment was provided by the striking difference in reactivity between VIII and IX with respect to reduction of the keto group. While IX reacts smoothly with NaBH_4 (as does V) to give the corresponding alcohol complex X (Scheme 2), VIII does not react under identical conditions, and decomposition or recovery of the starting material was observed. Models indicate that it is unlikely that conventional *exo* complexation of a $\text{Fe}(\text{CO})_3$ group is sterically compatible with a secondary alcohol group at C(9). A further explanation for the inertness of VIII could be the restricted access of the reducing agent to the keto group at C(9), the $\text{Fe}(\text{CO})_3$ entity acting as a protecting group.

SCHEME 2



The assignment of VIII and IX as the *exo* and *endo* isomers respectively, is also compatible with our explanation for the marked solvent effect observed in the stereospecific preparation. This must be induced by the high polarity of V arising from the presence of the keto group. As the *exo* compound is formed on using the nonpolar solvent benzene it is likely that under these conditions a preliminary attraction between $\text{Fe}_2(\text{CO})_9$ and the ketonic double bond occurs, and after further reaction steps establishes the *exo* configuration of VIII. A similar argument can be used to explain the stereospecific formation of IX when the reaction is carried out in the polar solvent methanol. Attraction of the iron carbonyl reactant by the keto group then seems much less likely, as interaction between $\text{Fe}_2(\text{CO})_9$ and methanol is more probable. Solvation of the keto group by methanol with the possible establishment of a hemiketal-ketal equilibrium, must also be taken into account. This makes the *exo* side of V virtually inaccessible, thus favouring the exclusive formation of IX under these conditions.

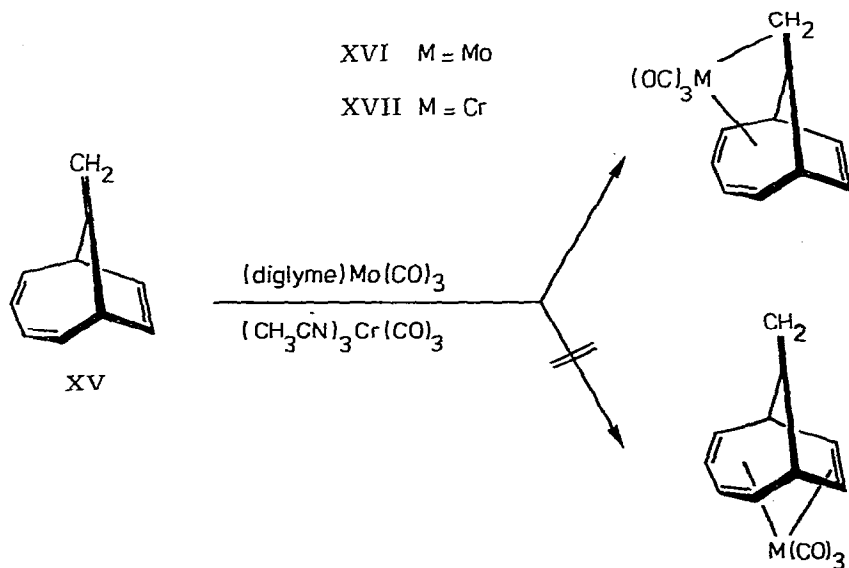
Solvent effects on the isomer distribution of olefinic complexes containing

heteroatoms have been noted previously [9]. The high selectivity induced by a heteroatom and reported here is, to our knowledge, unprecedented. It is not restricted, however, to V and its complexes, as is shown by the fact that we were unable to prepare the alcohol X by a direct route. When the uncomplexed alcohol [7] is treated with $\text{Fe}_2(\text{CO})_9$ under a variety of conditions a rather unstable red compound $\text{C}_9\text{H}_{10}\text{OFe}(\text{CO})_3$ (XI), not identical with the *endo* coordinated X, is isolated in low yields. The ^{13}C NMR spectrum indicates an unsymmetrical bonding mode in XI, as 9 signals are observed for the 9 ring carbons. It suggests that an unusual *exo* coordination must be present in XI, probably involving complexation to the hydroxy group in a manner not yet fully elucidated. Again interaction between $\text{Fe}_2(\text{CO})_9$ and the hydroxy group, which establishes the *exo* stereochemistry after further reaction steps, can be assumed to be the initial step.

In order to obtain other examples of *exo*–*endo* isomers we attempted catalytic hydrogenation of the uncomplexed double bond of VIII and IX. This proved equally feasible for both isomers, using a Pd/C catalyst at atmospheric pressure. The previously noted difference in chemical shifts is again observed in the hydrogenated species, with the signals for the *exo* isomer XII appearing at higher field than those for XIII (Fig. 1). The same reaction also occurs with complex X, to give the hydrogenated alcohol XIV (Scheme 2).

Another derivative of V is 9-methylenebicyclo[4.2.1]nona-2,4,7-triene (XV), prepared from V by a Wittig reaction [10]. However, because of the additional double bond it offers an alternative mode of bonding when coordinating over three double bonds. Apart from the conventional bonding type involving *endo* coordination to the bishomobenzene system formed by the 2,4-diene unit and the isolated cyclic double bond, a further possibility is *exo* coordination to the bishomofulvene moiety formed by the conjugated double bonds and the semicyclic double bond. The second bonding type has not been

SCHEME 3



observed before. Models of XV show that the two isolated double bonds are in approximately the same geometric position with respect to the 2,4-diene unit, but one lies parallel and the other perpendicular to it.

A rapid reaction is observed when XV is treated with (diglyme)Mo(CO)₃ or (CH₃CN)₃Cr(CO)₃ giving two crystalline solids XVI and XVII after workup (Scheme 3), which were characterised by elemental analysis, IR and NMR spectra (Table 1,2). Surprisingly, the ¹³C NMR spectra show both compounds to be *exo* isomers. Unusually large coordination shifts are observed for the quaternary carbon C(9) of the semicyclic double bond, i.e. 98 and 106 ppm for XVI and XVII, respectively. The corresponding shifts for the terminal carbon C(10) are only 40 and 37 ppm and in the normal range. It is possible that the large coordination shifts are indicative of a special bonding situation at C(9). At this stage we also do not know whether kinetic or thermodynamic factors favour the exclusive and unprecedented *exo* complexation in XVI and XVII over the conventional (and expected) *endo* mode observed in VI and VII. Compounds XVI and XVII represent yet a further example of selectivity in complex formation, governed by either steric or electronic factors. We are presently extending our investigations to other systems in order to gain additional insight into the detail of stereospecific organometallic reactions.

Experimental

All experiments were carried out under nitrogen, using solvents purified under nitrogen by standard procedures. NMR measurements were made on a Varian XL-100 and IR spectra were obtained on a Beckman IR 12. V was prepared according to [7], XV by the procedure described in [10]. ¹³C NMR of V (in C₆D₆): 211.9, 128.9, 124.8, 124.6, 52.3 ppm.

(a) VI, VII, XVI and XVII. Treatment of V or XV with (diglyme)Mo(CO)₃ or (CH₃CN)₃Cr(CO)₃ and workup as described generally in [3,4] yields yellow to red crystalline solids.

VI: Found: C, 46.34; H, 2.64; Mo, 30.43. C₁₂H₈O₄Mo calcd.: C, 46.17; H, 2.58; Mo, 30.74%.

VII: Found: C, 53.67; H, 3.36; Cr, 19.12. C₁₂H₈O₄Cr calcd.: C, 53.74; H, 3.00; Cr, 19.38%.

XVI: Found: C, 50.15; H, 3.21; Mo, 30.70. C₁₃H₁₀O₃Mo calcd.: C, 50.34; H, 3.25; Mo, 30.93%.

XVII: Found: C, 58.38; H, 3.66; Cr, 18.77. C₁₃H₁₀O₃Cr calcd.: C, 58.65; H, 3.78; Cr, 19.53%.

(b) VIII. V is treated with an excess of Fe₂(CO)₉ in benzene and heated for two hours at 60°C. After removal of the solvent and Fe(CO)₅ under vacuum the dry residue is extracted with hot hexane and filtered. After precipitation at -30°C VIII is recrystallised twice from hexane, giving yellow needles. Yield 55% (relative to V). Found: C, 53.20; H, 2.98. C₁₂H₈O₄Fe calcd.: C, 52.98; H, 2.96%.

(c) IX. V is stirred with an excess of Fe₂(CO)₉ in methanol at 30°C for two days. Evaporation of the solvent and Fe(CO)₅ under vacuum yields a solid residue which is extracted with ether and filtered. The yellow solution is concentrated and chromatographed through a 30 cm Alox column (activity grade III).

The major yellow fraction is collected and the solvent removed in vacuo. Repeated recrystallisation from n-hexane at -30°C gives yellow crystalline platelets. Yields 42% (relative to V). Found: C, 53.23; H, 3.03. $\text{C}_{12}\text{H}_8\text{O}_4\text{Fe}$ calcd.: C, 52.98; H, 2.96%.

(d) X. IX is treated with NaBH_4 in $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ as described in [7] for the free ketone. After removal of the solvent and dilution of the residue with water, X is extracted with ether and dried. Recrystallisation from hexane yields pale yellow needles, yield 85%. Found: C, 52.31; H, 3.91. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Fe}$ calcd.: C, 52.58; H, 3.68%.

(e) XI. V is reduced to the alcohol as described in [7]. This alcohol is treated with $\text{Fe}_2(\text{CO})_9$ in benzene at 60°C or methanol at 30°C as described above. After extractive workup as described in (b), a small yield (20%) of red crystals is obtained.

^{13}C NMR (in C_6D_6 , noise-decoupled, relative to TMS): 212.3, 210.7, 136.8, 131.6, 95.3, 94.2, 92.2, 61.5, 49.5, 45.9, 26.6 ppm. Found: C, 52.49; H, 3.36. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Fe}$ calcd.: C, 52.58; H, 3.68%.

(f) XII, XIII and XIV. VIII, IX and X are dissolved in n-hexane and a Pd/C catalyst (5% palladium) is added. The solution is flushed vigorously with H_2 and then kept stirring for two days under a constant pressure of 1 atm H_2 . After filtering over cotton wool and cooling to -30°C pale yellow crystals precipitate, yield 85–90%.

XII: Found: C, 52.47; H, 3.58; Fe, 20.50. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Fe}$ calcd.: C, 52.58; H, 3.68; Fe, 20.38%.

XIII: Found: C, 52.42; H, 3.57; Fe, 20.35. $\text{C}_{12}\text{H}_{10}\text{O}_4\text{Fe}$ calcd.: C, 52.58; H, 3.68; Fe, 20.38%.

XIV: Found: C, 52.11; H, 4.30; Fe, 20.03. $\text{C}_{12}\text{H}_{12}\text{O}_4\text{Fe}$ calcd.: C, 52.21; H, 4.38; Fe, 20.23%.

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