

Reactivity of Co-ordinated Ligands. Part XXV.¹ Tritylcyclo-octatetraene Derivatives of Tricarbonyliron and Protonation of Tricarbonyl(η -tritylcyclo-octatetraene)iron

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The protonation of tricarbonyl(η -tritylcyclo-octatetraene)iron, (VI), at 10 °C yields the cation tricarbonyl(1—5- η -6-tritylcyclo-octa-2,4,6-trienylium)iron, (IX). Tritylation of tricarbonyl(η -cyclo-octatetraene)iron, (IV), yields the cation tricarbonyl(1—5- η -8-tritylcyclo-octa-2,4,6-trienylium)iron, (V). Both cations have been observed by ¹³C and ¹H n.m.r. spectroscopy. Deprotonation of cations (V) and (IX) by base yields (VI). At 160 °C complex (VI) isomerizes to tricarbonyl(2,3:4,5- η -7-tritylbicyclo[4.2.0]octa-2,4,7-triene)iron, (VII). Reaction of complex (VI) or (VII) with Ce⁴⁺ in ethanol yields tritylcyclo-octatetraene, (VIII), in good yield. The ¹³C and ¹H n.m.r. spectra of (V)—(IX) are reported.

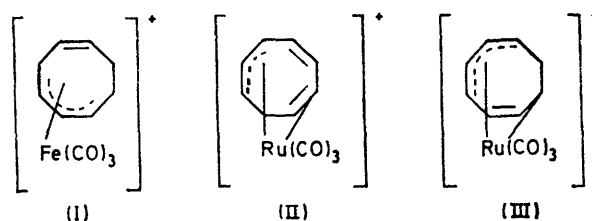
THE structures of molecules formed by protonation of cyclo-octatetraene (cot) co-ordinated to an iron, ruthenium, or osmium atom have been a matter of recent interest.²⁻⁵ Brookhart *et al.*³ reported that initially monocyclic 1—5- η co-ordinated cations (I) are formed from protonation of tricarbonyl(η -cyclo-octatetraene)iron and tricarbonyl(η -methylcyclo-octatetraene)iron at -120 °C; isomerization follows at -60 °C to give 2—6- η -bicyclo[5.1.0]octadienylium cations. Greco and his co-workers⁴ have reported the formation of monocyclic 1—5- η co-ordinated complexes of iron from intramolecular protonation of a cot molecule co-ordinated to an iron atom. Cooke *et al.*⁵ have protonated [(cot)Ru(CO)₃] and interpret the n.m.r. spectrum of

¹ Part XXIV, M. N. S. Hill, B. F. G. Johnson, T. Keating, and J. Lewis, *J. C. S. Dalton*, 1975, 1197.

² For a review see E. W. Abel and S. Tyfield, *Adv. Organometallic Chem.*, 1970, **8**, 117.

³ M. Brookhart, E. R. Davis, and D. L. Hunt, *J. Amer. Chem. Soc.*, 1972, **94**, 7853 and refs. therein.

the product as due to a C₈H₉ moiety bonded with either 1—3:6,7- η , (II), or 1- σ ,3—6- η bonding, (III).



The geometric requirements of an eight-membered ring having a 1—5- η group co-ordinated to an iron atom and a free double bond impose severe strain on the ring. If the 1—5- η group is planar then severe torsional strain is expected on the unco-ordinated double bond. The

⁴ A. Greco, A. Carbonaro, F. Cambisi, and G. Dall'Asta, *Chimica e Industria*, 1970, **52**, 877.

⁵ M. Cooke, P. T. Draggett, M. Green, B. F. G. Johnson, J. Lewis, and D. J. Yarrow, *Chem. Comm.*, 1971, 621.

reported ^1H n.m.r. spectra^{3,4} of monocyclic 1-5- η co-ordinated species are not totally convincing, in that a possible structure containing co-ordinated allyl and olefin groups along with an unco-ordinated olefin was not considered. Such a structure would allow relief of much strain and would be compatible with the observed spectra. Also, many of the protons in the n.m.r. spectra have identical chemical shifts and only a limited number of coupling constants could be observed.

Complexes of substituted cyclo-octatetraenes with metal carbonyls, $\text{M}(\text{CO})_n$, often show fluxional behaviour.⁶⁻⁸ A very large substituent such as triphenylmethyl (trityl) may alter the rate or even the nature of the process responsible for fluxional behaviour. Alternatively, the very large trityl substituent may stabilize a structure fundamentally different from that of the cot-like complexes. The large trityl group causes appreciable shift in the n.m.r. frequencies of some of the protons on the cot ring, greatly aiding the analysis of the spectra of the complexes which we prepared.

In this paper we report the structures of two new monocyclic 1-5- η co-ordinated derivatives of $[(\text{cot})\text{Fe}(\text{CO})_3]$. We also report two isomers of $[(\text{tcot})\text{Fe}(\text{CO})_3]$ (tcot = tritylcyclo-octatetraene). One is a monocyclic fluxional molecule, the other a rigid bicyclo[4.2.0]octatriene. In addition we have also prepared tcot and find it to have a rigid structure.

EXPERIMENTAL

Microanalyses were by the Microanalytical Department of the University Chemical Laboratory, Cambridge. ^1H N.m.r. spectra were obtained with Perkin-Elmer R12B (60 MHz) and Varian Associates XL-100 instruments (100 MHz), ^{13}C n.m.r. spectra on a Varian Associates XL-100 spectrometer. I.r. spectra were recorded with a Perkin-Elmer 257 instrument. M.p.s were measured in open capillary tubes on a Gallenkamp apparatus and were uncorrected.

Tricarbonyl(1-5- η -8-tritylcyclo-octa-2,4,6-trienylium)iron Tetrafluoroborate (V).—Tricarbonyl(η -cyclo-octatetraene)iron, (IV), (669 mg)⁹ was dissolved in CH_2Cl_2 (10 cm^3) under a nitrogen atmosphere in a reaction flask. Triphenylmethylmethyl tetrafluoroborate¹⁰ (904 mg) dissolved in CH_2Cl_2 (5 cm^3) was added with stirring. A yellow solid precipitated. Anhydrous diethyl ether (15 cm^3) was added to complete precipitation. The precipitate was filtered off and washed with diethyl ether [yield 1.072 g, 81% corresponding to complex (V)]. For analysis the material was reprecipitated from dichloromethane and diethyl ether and then dried *in vacuo* at 80 °C for 4 h (Found: C, 58.7; H, 3.95. Calc. for $\text{C}_{30}\text{H}_{23}\text{BF}_4\text{FeO}_3$: C, 62.7; H, 4.00%), i.r. bands at 2 128 and 2 083 cm^{-1} (Nujol mull) in the $\nu(\text{C}=\text{O})$ region.

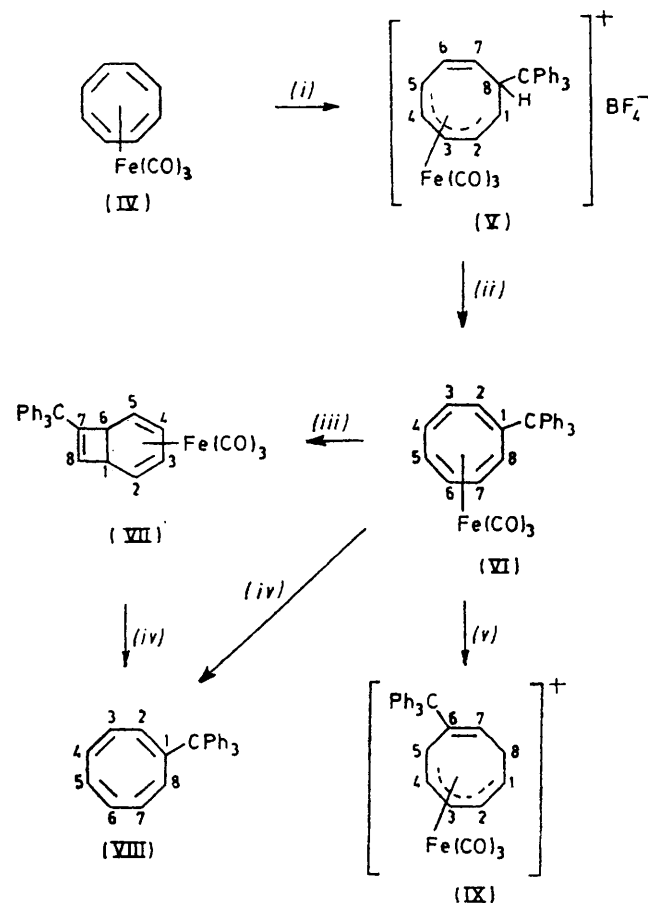
Tricarbonyl(η -tritylcyclo-octatetraene)iron, (VI).—Complex (V) (1.00 g) was added as a solid with stirring to a solution of triethylamine (1.0 g) in dichloromethane (100 cm^3). The solution was initially yellow but soon became dark brown. The solvent and excess of triethylamine were

⁶ F. A. Cotton, A. Davison, T. J. Marks, and A. Musco, *J. Amer. Chem. Soc.*, 1969, **91**, 6598.

⁷ F. A. Cotton, *Accounts Chem. Res.*, 1968, **1**, 257.

⁸ B. F. G. Johnson, J. Lewis, and G. L. P. Randall, *J. Chem. Soc. (A)*, 1971, 422.

evaporated and the product dissolved in hexane. The product was then placed on a silica column and eluted with 10% dichloromethane in hexane. A dark red band contained the product (VI) (622 mg, 74%) which was further purified by crystallization from hexane at -20 °C and drying of the crystals *in vacuo* at 80 °C for 12 h (Found: C, 73.75; H, 4.40. Calc. for $\text{C}_{30}\text{H}_{22}\text{FeO}_3$: C, 74.1; H, 4.55%), i.r. bands at 2 060, 1 998, and 1 985 cm^{-1} (hexane solution) in the $\nu(\text{C}=\text{O})$ region.



(i), $[\text{Ph}_3\text{C}][\text{BF}_4]$ in CH_2Cl_2 ; (ii), Et_3N in CH_2Cl_2 or $(\text{MeO})\text{Na}$ in MeOH ; (iii), 160 °C *in vacuo*; (iv), $[\text{NH}_4]_2[\text{Ce}(\text{NO}_3)_6]$ in EtOH ; (v), $\text{CF}_3\text{CO}_2\text{H}$ in CD_2Cl_2 .

Alternatively, complex (VI) was obtained by addition of (V) (4.0 g) to a solution of sodium methoxide (3.0 g) in methanol (AnalaR, 150 cm^3). Complex (V) dissolved quickly to give a yellow solution. After a few minutes this solution became red, and after 15 min produced an orange precipitate. The product was placed on a silica column and eluted with dichloromethane to remove ionic impurities. It was purified as above (2.01 g, 59%).

Tricarbonyl(2,3:4,5- η -7-tritylbicyclo[4.2.0]octa-2,4,7-triene)iron, (VII).—Complex (VI) was heated to 160 °C *in vacuo*. At this temperature the red solid melted to give a clear, pale yellow, liquid with some dark decomposition products. The liquid solidified on cooling. The resulting solid was dissolved in dichloromethane, eluted through a silica

⁹ T. A. Manuel and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 366.

¹⁰ H. J. Dauben, jun., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 1960, **25**, 1442.

column with dichloromethane, and recrystallized from hexane. The yellow crystalline solid *product* (VII) was kept under vacuum for 12 h at 80 °C to remove solvent, yield 80% from (VI) (Found: C, 73.65; H, 4.30. Calc. for $C_{30}H_{22}FeO_3$: C, 74.1; H, 4.55%), i.r. bands at 2 053, 1 985, and 1 978 cm^{-1} (hexane solution) in the $\nu(C=O)$ region.

Tricarbonyl(1—5- η -6-tritylcyclo-octa-2,4,6-trienylium)iron Cation, (IX).—Complex (VI) was dissolved in CD_2Cl_2 in an n.m.r. tube. The sample was cooled to 0 °C. A volume of trifluoroacetic acid equal to approximately one fifth the volume of the CD_2Cl_2 was added to the n.m.r. tube. The tube was capped and then shaken to mix the substances, keeping the temperature of the tube near 0 °C. The tube was quickly placed into a n.m.r. spinner and probe which had been precooled to 0 °C. N.m.r. spectra were run at 10 °C.

Tritylcyclo-octatetraene, (VIII).—Complex (VI) (86 mg) was dissolved in absolute ethanol (18 cm^3). Ammonium hexanitratocerate(IV) (300 mg) dissolved in a minimum of absolute ethanol was then added dropwise. After all of the cerium reagent had been added, water (100 cm^3) was added to the solution which became cloudy white. The mixture was extracted with diethyl ether (4×50 cm^3) and the ether layer was dried over $MgSO_4$, filtered, and the ether evaporated. The product was dissolved in hexane, placed on a silica column, and eluted with benzene. The solvent was removed *in vacuo* and the *product* crystallized from hexane and dried *in vacuo* at 80 °C for 4 h as pale greenish yellow crystals, (VIII) (Found: C, 93.5; H, 6.45. Calc. for $C_{27}H_{22}$: C, 93.6; H, 6.35%). The compound could be similarly prepared from complex (VII).

RESULTS AND DISCUSSION

The reaction of triphenylmethylm tetrafluoroborate with $[(cot)Fe(CO)_3]$, (IV), in dichloromethane gave tricarbonyl(1—5- η -8-tritylcyclo-octa-2,4,6-trienylium)iron, (V) (80%), identified on the basis of n.m.r. data (Tables 1 and 2) and the product of its reaction with base. Complex (V) reacted with base to give tricarbonyl-(η -tritylcyclo-octatetraene)iron, (VI) (70%), which was identified by spectroscopic and analytical data. The hydrogen analysis for complex (V) was correct, but the carbon analysis was always low, a common observation for tetrafluoroborate salts. From its 1H and ^{13}C n.m.r. spectra (Tables 3 and 4), complex (VI) is a fluxional molecule and maintains its fluxional behaviour down to -80 °C. The rather large trityl group does not inhibit this behaviour.

When a solution of complex (VI) in deuteriodichloromethane at 10 °C was protonated by trifluoroacetic acid, a monocyclic 1—5- η co-ordinated cation, (IX), was the major product (*ca.* 80%). The latter was identified by its 1H and ^{13}C n.m.r. spectra (Tables 1 and 2) and proton-decoupling experiments. The identity of the minor component was not established. On neutralization of the acid solution of (IX) with trimethylamine, the cation disappeared and in its place substantial quantities of (VI) could be identified together with (IV), (VIII), and some unidentified substances.

The possibility that (IX) was a bicyclic cation was easily eliminated by ^{13}C n.m.r. spectroscopy. A bicyclic

ion would have three sp^3 carbon atoms. Only one carbon atom with an attached proton had a chemical shift in the sp^3 region. Seven different resonances were well separated for the ring (eight-membered) protons and gave the appropriate intensities. Position 8 had a relative intensity of 2 with a protonic acid and 1 with a deuterio-acid. 1H N.m.r. decoupling experiments showed that the coupling order was 5,4,3,2,1,8,7. When the proton going on at position 8 was replaced by a deuteron the n.m.r. spectra of protons 1 and 7 simplified in the expected manner. The shift equivalence of the *endo*- and *exo*-protons on position 8 is the same as found by Brookhart *et al.*³ for ion (I). That the methylene protons are stereochemically very different is shown by the difference in $J(H_7-H_8)$ between the protonated species (4.0 Hz) and the deuterated species (2.75 Hz). Our observed chemical shifts for complex (IX) correlate reasonably well with the values reported for (I).³ The coupling constants $J(H_1-H_2)$, $J(H_2-H_3)$, and $J(H_3-H_4)$ are almost identical for ions (IX) and (I). Our values of $J(H_1-H_8)$, $J(H_4-H_5)$, and $J(H_7-H_8)$ are all reasonable for the structure proposed.

The ^{13}C n.m.r. data cannot be interpreted in the same direct manner as the 1H data because ^{13}C spectra of model dienylmetal systems have not been previously reported. The carbon atom at position 8 can be assigned as sp^3 from its chemical shift (28.2 p.p.m.); C_7 must be under the trityl peaks, as it would be observable anywhere else. Thus C_6 and C_7 can be assigned as unco-ordinated olefin carbon atoms. Carbon atoms 1—5 had a series of chemical shifts which are very compatible with a dienyl assignment. Any attempt to interpret the ^{13}C n.m.r. spectrum in terms of a co-ordinated allyl or diene group leads to unreasonable chemical shifts for some of the carbon atoms.

The structure of ion (V) is best deduced by comparison of its n.m.r. spectra with those of (IX) (Tables 1 and 2). Four of the protons in complex (V) had similar chemical shifts. The complex overlapping of these peaks made a complete analysis impossible. However, protons 1, 3, 5, and 8 were well separated and resolved. In addition, decoupling experiments gave chemical shifts for protons 2, 4, 6, and 7. If the proton spectrum of complex (V) is assigned on the basis of a structure analogous to (IX), very reasonable chemical shifts are obtained and the observable coupling constants are very similar to those of (IX) and (I). Only proton 8 has an appreciably different chemical shift, as would be expected with a trityl group on C_8 . The ^{13}C n.m.r. spectrum of (V) was almost identical to that of (IX). The carbon atom at position 8 had a greater chemical shift (47.4 as against 28.2 p.p.m. from $SiMe_4$), as would have been expected for adding a trityl group at this position; C_6 is less shielded in complex (V) (123.2 p.p.m.) because it does not have a trityl group [136.6 p.p.m. in (IX)]. Otherwise the correspondence of the carbon resonance is striking. For complex (IX) the ^{13}C n.m.r. spectrum of the trityl group could be assigned, but for (V) the trityl resonance was a complex multiplet

TABLE 1
 ^1H N.m.r. data for ions (V), (IX), and (I)

Ion	τ^a									J/Hz
	trityl	H ₁	H ₂	H ₃	H ₄	H ₅	H ₆	H ₇	H ₈	
(V) ^b	2.6	5.0 (dd)	3.75 (m)	3.46 (t)	4.0 (m)	5.25 (dd)	4.05 (m)	3.9 (m)	4.52 (d)	$J(\text{H}_1-\text{H}_2)$ 9.5, $J(\text{H}_1-\text{H}_8)$ 5.1, $J(\text{H}_5-\text{H}_3) = J(\text{H}_3-\text{H}_4)$ 7, $J(\text{H}_4-\text{H}_5)$ 10, $J(\text{H}_4-\text{H}_6)$ 6.5
(IX) ^c	2.6	5.3 (bm) [dd]	4.08 (dd)	3.25 (t)	4.80 (dd)	5.79 (d)		3.75 (t) [d]	6.72 (bm)	$J(\text{H}_1-\text{H}_2)$ 10.0, $J(\text{H}_1-\text{H}_8)$ [5.75], $J(\text{H}_2-\text{H}_3)$ [7.5], $J(\text{H}_3-\text{H}_4)$ 7.0, $J(\text{H}_4-\text{H}_5)$ 10.0, $J(\text{H}_7-\text{H}_8)$ 4.0 [2.75]
(I) ^d		5.42	4.05	3.10	4.05	5.42	4.05	4.05	7.1	$J(\text{H}_3-\text{H}_2) = J(\text{H}_3-\text{H}_4)$ 7, $J(\text{H}_1-\text{H}_2)$ 10

^a Chemical shifts were measured relative to solvent deuterium lock and converted to τ values in the same solvent. d = Doublet, dd = doublet of doublets, t = triplet, m = multiplet, bm = broad multiplet. Data in square brackets were recorded in deuterio-trifluoroacetic acid. ^b Spectra were run in perdeuterioacetone at 0 °C. ^c Spectra were run in CD₂Cl₂ + trifluoroacetic acid at 10 °C. ^d Data from ref. 3.

TABLE 2
 ^{13}C N.m.r. data for ions (IX) and (V)

Ion	$\delta^a/\text{p.p.m.}$												
	trityl					C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
(IX) ^b	C(sp ³)	C ₁	<i>o</i>	<i>m</i>	<i>p</i>	74.9	98.7	106.2	95.5	73.7	136.6	under trityl	28.2
(V) ^c			← 124—129 →			71.0	99.6	104.3	96.4	69.6	123.2	under trityl	47.4

^a Chemical shifts were measured relative to solvent deuterium lock and converted to p.p.m. from SiMe₄ in the same solvent. ^b Spectra were run in deuteriodichloromethane plus trifluoroacetic acid at 10 °C. ^c Spectra run in perdeuterioacetone at 0 °C.

TABLE 3
 ^1H N.m.r. data for compounds (VI) and (VIII)

Compound	τ^a						J^b/Hz
	trityl	H ₂ , H ₈	H ₃ , H ₇	H ₄ , H ₆	H ₅		
(VI)	2.72 (m)	4.26 (d)	4.92 (t)	5.37 (t)	5.62 (t)		$J(\text{H}_2-\text{H}_3)$ 11.4, $J(\text{H}_3-\text{H}_4)$ 9, $J(\text{H}_4-\text{H}_5)$ 7.7
15 ^c		2	2.1	← 2.9 →			
(VIII)	trityl						$J(\text{H}_7-\text{H}_8)$ 11.5
	<i>o</i>	<i>m</i>	<i>p</i>				
	2.55	2.70	2.75	4.0 (s)	4.14 (s)	4.25 (s)	4.38 (d)
	← 15 ^c →			3	2	1	1

^a Spectra were run at room temperature in deuteriochloroform. Chemical shifts were measured relative to solvent deuterium lock and converted to τ values in the same solvent. s = Singlet. ^b For complex (VI) a reasonable computer fit was obtained by assuming that all H-H couplings through four bonds were < 0.8 Hz. ^c Relative intensity.

TABLE 4
 ^{13}C N.m.r. data for compounds (VI) and (VIII)

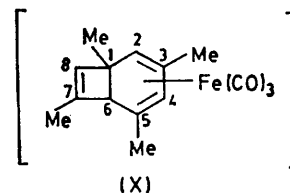
Compound	$\delta^a/\text{p.p.m.}$									
	trityl					C ₁	C ₂ , C ₈	C ₃ , C ₇	C ₄ , C ₆	C ₅
(VI)	C(sp ³)	C ₁	<i>o</i>	<i>m</i>	<i>p</i>	140.7	117.9	96.7	85.4	80.8
(VIII)	65.9	144.5	127.2 ^b	130.8 ^c	125.6	147.7	130.2	131.2	131.8	132.3
							132.4	132.5	135.2	

^a Spectra were run at room temperature in deuteriochloroform. Chemical shifts were measured relative to solvent deuterium lock and converted to p.p.m. from SiMe₄ in the same solvent. ^b The attached protons appeared at τ 2.70. ^c The attached protons appeared at τ 2.55.

which could not be resolved. This may indicate that in complex (V) the rotation of the trityl group is restricted and the phenyl groups lose their equivalence.

At 160 °C complex (VI) isomerized to give the bicyclic system (VII) in good yield (80%). Complex (VII) was identified by spectroscopic and analytical data; n.m.r. data are summarized in Tables 5 and 6. Proton-decoupling experiments showed that the coupling in complex (VII) is cyclic (1,2,3,4,5,6) with a six-membered ring. The proton at position 8 was not coupled to any other proton in the molecule. If a model of the suggested structure is constructed, it is seen that the dihedral angle between H_8 and H_1 is near 90°; thus, the lack of coupling is reasonable.¹¹ The absolute

48.7 p.p.m.). The co-ordinated diene has chemical shifts similar to other such systems [cf. for (η -buta-1,3-diene)tricarbonyliron¹⁴ $\delta(\text{CH})$ 86.7 and $\delta(\text{CH}_2)$ 42.0 p.p.m.].



When treated with Ce^{IV} in ethanol, both complexes (VI) and (VII) gave tritylcyclo-octatetraene, (VIII)

TABLE 5
¹H N.m.r. data for complexes (VII) and (X)

Complex	τ^a								J/Hz	
	trityl	H_1	H_2	H_3	H_4	H_5	H_6	H_7		H_8
(VII)	2.8 (m)	7.00 (t)	6.77 (m)	4.71 (t)	5.07 (t)	7.33 (t)	6.75 (m)		4.00 (s)	$J(H_1-H_2) = J(H_3-H_4) =$ $J(H_5-H_6) = J(H_1-H_6) =$ 4.5, $J(H_2-H_3) =$ $J(H_4-H_5) = 6.0$, $J(H_2-H_4) =$ $J(H_3-H_5) = 1.5$, $J(H_1-H_2) \sim J(H_1-H_4)$ $\sim J(H_4-H_6) \text{ ca. } 1$
(X) ^b		7.23		4.78		7.70		4.24		

^a Spectra were run at room temperature in deuteriochloroform. Chemical shifts were measured relative to solvent deuterium lock and converted to τ values in the same solvent. ^b Data from ref. 13. The methyl protons are at τ 7.92–8.77.

TABLE 6
¹³C N.m.r. data for complex (VII)
 $\delta^*/\text{p.p.m.}$

$\text{C}(sp^3)$	trityl			C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	CO	
	C_1	o	m										p
61.1	143.9	127.2	130.2	126.0	47.2	64.3	85.2	86.4	63.3	48.7	158.8	139.5	211.0

* Spectra were run at room temperature in deuteriochloroform. Chemical shifts were measured relative to solvent deuterium lock and converted to p.p.m. from SiMe_4 in the same solvent.

assignment of the spectrum (*i.e.* which bridgehead proton is adjacent to the trityl group) was accomplished by carrying out an Overhauser-enhancement experiment; ¹² H_8 was irradiated while the intensities of the other peaks were monitored. Bridgehead proton H_1 was enhanced by *ca.* 15%. In addition, protons 6, 5, 2, and 1 were irradiated in turn while monitoring the resonance of 8. When H_1 was irradiated the intensity of H_8 was enhanced by *ca.* 15%; when the other protons were irradiated no change was observed in H_8 . Thus, H_1 must be the spatially closest proton to H_8 . Cotton and Musco¹³ have prepared a compound which they suggest contains co-ordinated 1,3,5,7-tetramethylbicyclo[4.2.0]octa-2,4,7-triene (X). The correspondence of the ¹H n.m.r. spectra of complexes (VII) and (X) is shown in Table 5. The ¹³C n.m.r. spectrum of complex (VII) (Table 6) clearly shows the bridgehead carbon atoms (1 and 6) as having sp^3 hybridization (δ 42.7 and

ca. 80%), identified by chemical analysis, mass (Table 7) and n.m.r. spectroscopy. Very weak i.r. bands at 1 600 and 1 645 cm^{-1} can be assigned to double bonds. The ¹H n.m.r. spectrum of compound (VIII) (Table 3) showed only peaks in the phenyl and olefin regions with ratios of total intensities very close to 15 : 7. 100 and 60 MHz ¹H n.m.r. spectra were compared to determine which splittings were due to spin-spin coupling. Only one such splitting could be observed in the olefin region. The single proton at τ 4.38 was split into a doublet (J 11.5 Hz). The existence of a unique proton with only one adjacent proton in the molecule indicates that the cyclo-octatetraene ring is in a rigid conformation. The unique proton is probably at the 8 position. The ¹³C n.m.r. spectrum (Table 5) is totally consistent with a rigid cyclo-octatetraene ring. In addition to the trityl carbons, eight different carbon atoms could be identified in the olefin region. Studies of the ¹H n.m.r. spectrum

¹¹ H. Booth, *Progr. N.M.R. Spectroscopy*, 1969, **5**, 160–162.

¹² J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, 1965, vol. 1, p. 116.

¹³ F. A. Cotton and A. Musco, *J. Amer. Chem. Soc.*, 1968, **90**, 1444.

¹⁴ H. L. Retcofsky, E. N. Frankel, and H. S. Gutowsky, *J. Amer. Chem. Soc.*, 1966, **88**, 1585.

as a function of temperature from +50 to -50 °C showed only small changes in chemical shift of some of the olefin peaks. At 50 °C the doublet moved slightly to higher field (τ 4.48) and the other three peaks moved slightly to lower field. The peak at τ 4.0 also began to split into two peaks at -50 °C (τ 3.89 and 3.96,

electrons to the iron. A trityl group would have no such effect and because of its bulk would be expected to take up a less hindered position. The ring closure of complex (VI) to (VII) is one of the few reported cases of electrocyclic ring closure of an organic ligand bound to a transition metal.³ The stability of complex (VII)

TABLE 7
Mass-spectral data

Compound	<i>M</i>	<i>m/e</i> (major ions)	Assignment	Metastable transition	Assignment	
(VI)	486	486	<i>P</i>	351.5	$(P - 3CO) \rightarrow (P - 3CO - C_2H_2)$	
		458	<i>P</i> - CO	261.5	$(P - 3CO) \rightarrow (P - 3CO - C_6H_6)$	
		430	<i>P</i> - 2CO			
		402	<i>P</i> - 3CO			
		376	<i>P</i> - 3CO - C ₂ H ₂			
		346	<i>P</i> - 3CO - Fe			
(VII)	486	486	<i>P</i>	261	$(P - 3CO) \rightarrow (P - 3CO - C_6H_6)$	
		430	<i>P</i> - 2CO			
		402	<i>P</i> - 3CO			
		376	<i>P</i> - 3CO - C ₂ H ₂			
		346	<i>P</i> - 3CO - Fe			
(VIII)	346	346	<i>P</i>	316.5	$P \rightarrow (P - CH_3)$	
		331	<i>P</i> - CH ₃	207.5	$P \rightarrow (P - C_6H_6)$	
		317	<i>P</i> - C ₂ H ₃			
		305	<i>P</i> - C ₃ H ₅			
		280	<i>P</i> - C ₅ H ₈			
		268	<i>P</i> - C ₆ H ₆			
		255	<i>P</i> - C ₇ H ₇			
		243	<i>P</i> - C ₈ H ₇			

rel. intensity *ca.* 2 : 1). At 50 °C no appreciable change in the spectrum was observed relative to the spectrum at room temperature.

Our results confirm the observations of Brookhart *et al.*³ The protonation of [(cot)Fe(CO)₃], (IV), or its methyl or trityl derivatives yields initially a dienyl co-ordinated cation. In addition the attack of a triphenylmethyl cation on (IV) gives a monocyclic dienyl co-ordinated cation. In complex (IX) the trityl group is at position 6, whereas in the methyl analogues the substituent is at the 3 or 4 position. The methyl group may enhance the ability of the dienyl group to donate

is strongly related to the co-ordination of the diene group to the iron atom. When the iron tricarbonyl is removed the ring system opens to reform the eight-membered cyclo-octatetraene ring. Despite the very large trityl group in complex (VI) the molecule is fluxional. In contrast, the unco-ordinated molecule (VIII) is rigid on the n.m.r. time scale, presumably in a boat form.

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