of compounds $(COT)M(CO)_3$ (M = Cr, Mo, W), King estimated E_a's of 6.0, 5.8, and 7.2 kcal/mole, respectively, by applying the Gutowsky–Holm[23] treatment to two of the lines, each subject to appreciable coupling effects, in the low-temperature spectra. King also obtained frequency factors in the range 4.5–16.1 $\times 10^5$ sec^{-1}. Although these parameters *might* refer to a 1,3 shift (without bond shift) rather than the 1,2 shift (with bond shift) corresponding to the phase-one activation parameters calculated in this work for the tetramethyl derivative, and even though one might expect on the basis of steric interactions a slightly higher activation energy for the tetramethyl derivative, a discrepancy of $\sim$10 kcal/mole between the activation energies for the $(COT)M(CO)_3$ compounds on the one hand and the $(TMCOT)M(CO)_3$ compounds on the other seems to deserve some comment. As pointed out by Allerhand, *et al.*,[24] one must use care not to apply equations relating line shapes to rates under certain simple circumstances in more complex circumstances where they do not hold. The Gutowsky–Holm treatment applies rigorously only to a system in which there are two spins exchanging with each other but not coupled. In $(C_8H_8)M(CO)_3$ molecules this is far from the case; there, eight spins are being permuted among four different environments with large coupling effects evident. It would not be surprising, then, to find large systematic errors in results calculated by application of the Gutowsky–Holm treatment in these cases. In particular, it can be seen that, if one neglects coupling, at slow exchange rates the apparent rate calculated from the spectra is greater than the true rate. At intermediate and faster exchange rates this error becomes progressively smaller. The effect upon the Arrhenius calculation is that E_a and log A will both be low. Hence it is hard to say what, if any, significance there is to the apparent difference between the activation parameters for the COT and TMCOT compounds.

Acknowledgment. We thank Mr. Josef Takats for his help in preparing the 1,3,5,7-tetramethylcyclooctatetraene.

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Stereochemically Nonrigid Organometallic Molecules. XIII. Preparation of 1,3,5,7-Tetramethylcyclooctatetraene Derivatives of the Iron Carbonyls[1,2]

F. A. Cotton and A. Musco[3]

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. *Received September 23, 1967*

Abstract: The reactions of $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ with 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) have been investigated. Using octane (bp 125°) as the reaction medium, four different compounds have been isolated and characterized. I is a yellow oil, thought to be (1,3,5,7-tetramethylbicyclo[4.2.0]octa-2,4,7-triene)iron tricarbonyl. II, a yellow solid, $(TMCOT)Fe_2(CO)_6$, is considered to be the TMCOT analog of *trans*-$(COT)[Fe(CO)_3]_2$. III, red crystals analyzing as $C_{12}H_{16}Fe_2(CO)_5$, obtained only in minute quantities, contains a tautomer of TMCOT as shown by an X-ray study reported elsewhere. IV, black crystals also analyzing as $C_{12}H_{16}Fe_2(CO)_5$, is a fluxional molecule analogous in structure (as shown by an X-ray study reported elsewhere) to the compound $(COT)Fe_2(CO)_5$ previously reported by Pettit and structurally characterized by Fleischer. Finally, by reaction of TMCOT with $Fe_2(CO)_9$ in refluxing hexane (bp 69°), orange crystals of a compound, $(TMCOT)Fe_2(CO)_6$, which is apparently analogous to Pettit's *cis*-$(COT)[Fe(CO)_3]_2$, are obtained. The compound $(TMCOT)Fe(CO)_3$ was not isolated.

The complexes formed by cyclooctatetraene (COT) with metal carbonyl moieties, $M_m(CO)_c$, have aroused considerable interest recently,[4–14] particularly because a number of then are fluxional. It has been shown[2] that the use of 1,3,5,7-tetramethylcyclooctatetraene (TMCOT) in place of COT may lead to similar or analogous compounds in which the replacement of alternating hydrogen atoms by methyl groups may have some useful consequences, such as altering the rate or even the qualitative nature of the processes responsible for fluxional behavior and effecting a desirable simplification in the limiting low-temperature

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[1] Research supported by the National Science Foundation and the Sloan Research Fund of MIT.

[2] Preceeding paper in this series, part XII: F. A. Cotton, J. W. Faller, and A. Musco, *J. Am. Chem. Soc.*, 90, 1438 (1968).

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spectra of the fluxional molecules. Another point of interest in studying TMCOT analogs of $(COT)M_m(CO)_c$ molecules is whether, on occasion, TMCOT compounds having fundamentally different structures may be obtained instead of or in addition to the COT-like compounds.

In view of the fact that some extremely interesting $(COT)Fe_n(CO)_c$ compounds have been reported[4,9] but not, in several instances structurally characterized, it was considered worthwhile to attempt the preparation and study of some homologous $(TMCOT)Fe_n(CO)_c$ compounds. A point of particular interest was the behavior of a TMCOT homolog of the fluxional molecule $(COT)Fe(CO)_3$.

Our investigation of $(TMCOT)Fe_n(CO)_c$ compounds is described in this paper, which covers the preparation of compounds, and in the two following papers which report single-crystal, X-ray studies of two of the compounds.[15,16] The study of TMCOT analogs of $(COT)Fe_n(CO)_c$ molecules was not carried to the fullest possible extent because (a) the preparation of large quantities of TMCOT is very arduous and (b), more important, our studies[13b,17] of the $(COT)Re_n(CO)_c$ compounds proved to be more facile and more informative and were thus given priority.

Experimental Section

The method of preparing 1,3,5,7-tetramethylcyclooctatetraene was that of de Mayo and Yip[18] with slight modifications as noted previously.[2]

Melting points are uncorrected. Microanalyses were by S. M. Nagy, MIT, and Galbraith Microanalytic Laboratory, Knoxville, Tenn. Infrared spectra were recorded on a Perkin-Elmer Infracord equipped with a grating, nmr spectra on a Varian Associates A60 spectrometer, and uv spectra on a Cary 14 spectrometer.

Reaction of TMCOT with $Fe_3(CO)_{12}$ in Octane. A mixture of 3 g (18 mmoles) of TMCOT and 2.6 g (5.1 mmoles) of $Fe_3(CO)_{12}$ in 100 ml of dry, oxygen-free octane was refluxed under nitrogen for 60 hr. The dark reaction mixture was cooled to room temperature and filtered under nitrogen. The solid residue was discarded. The reddish filtrate was evaporated at 25° (~0.05 torr) to give a red oil. Unreacted TMCOT (1.65 g) was recovered by sublimation at 45° (~0.05 torr).

The remaining red oil was then separated into its components by chromatography on alumina, using petroleum ether (boiling range 37–51°) as the eluting agent. Three distinct bands developed on the column, their colors being yellow, red, and brown.

The yellow band was first eluted with petroleum ether. Upon evaporation of the solvent, about 1.0 g of a yellow oil (I) was obtained. The oil was purified by distillation at 60° (0.05 torr). Its freezing point is below −70°.

Anal. Calcd for $C_{15}H_{16}FeO_3$ (*i.e.*, $C_{12}H_{16}Fe(CO)_3$): C, 60.02; H, 5.37. Found: C, 59.5; H, 5.28.

The red band was then eluted with petroleum ether and benzene (1:1 by volume). The mixed solvent was pumped off and the residual red oil was taken up in a few drops of petroleum ether. By cooling at −70° a few red crystals of III (~15 mg) were obtained, mp 100–102° dec.

Anal. Calcd for $C_{17}H_{16}Fe_2O_5$ (*i.e.*, $C_{12}H_{16}Fe_2(CO)_5$): C, 49.56; H, 3.92. Found: C, 49.7; H, 3.55.

The brown band was then eluted with petroleum ether and benzene (1:1 by volume). Upon evaporation of this solution a few black crystals (~15 mg) were obtained. These crystals had an infrared spectrum identical with that of the black crystals obtained from reaction of $Fe_2(CO)_9$ with TMCOT (*vide infra*) and were thus identified as compound IV.

Reaction of TMCOT with $Fe_2(CO)_9$ in Octane. A mixture of 1 g (6 mmoles) of TMCOT and 7 g (19 mmoles) of $Fe_2(CO)_9$ in 40 ml of dry, oxygen-free octane was refluxed under nitrogen for 2 hr. The brown reaction mixture was filtered under nitrogen at room temperature. The solid residue was discarded and the brown filtrate was evaporated at 25° (0.05 torr) to yield a brown solid residue. This residue was separated by chromatography on alumina using petroleum ether (boiling range 37–51°) as the eluent. Three well-defined bands, yellow, red, and dark brown in color, were formed.

The yellow band was eluted first using petroleum ether. When the solution was concentrated, yellow crystals (~80 mg) of compound II separated, mp ~132° dec.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$ (*i.e.*, $C_{12}H_{16}Fe_2(CO)_6$): C, 49.13; H, 3.67. Found: C, 49.0; H, 3.69.

The red band was next to be eluted by petroleum ether. After the eluting solvent was evaporated, there remained a red oil which was taken up in a few drops of petroleum ether. By cooling at −70° this solution yielded a few red crystals which had an infrared spectrum identical with that of the red crystals obtained by reaction of TMCOT with $Fe_3(CO)_{12}$ (*vide supra*) and were thus identified as compound III.

The third, dark brown band was eluted with benzene. Upon evaporation of the solvent, about 150 mg of black crystals (compound IV) was obtained. These crystals were recrystallized from a mixture of benzene and petroleum ether, mp 145° dec.

Anal. Calcd for $C_{17}H_{16}Fe_2O_5$ (*i.e.*, $C_{12}H_{16}Fe_2(CO)_5$): C, 49.56; H, 3.92. Found: C, 49.3; H, 4.03.

Reaction of TMCOT with $Fe_2(CO)_9$ in Hexane. Iron enneacarbonyl (2 g, 5.5 mmoles) and TMCOT (0.5 g, 3.1 mmoles) were added to 100 ml of hexane, and the mixture was refluxed gently for 2 hr. The solvent was removed with a water pump at 25°. The solid residue was extracted with light petroleum (37–51°) and the solution chromatographed on alumina. A fraction containing an orange band was isolated, and upon evaporation orange-brown crystals of compound V were obtained, yield ~50 mg.

Anal. Calcd for $C_{18}H_{16}Fe_2O_6$ (*i.e.*, $C_{12}H_{16}Fe_2(CO)_6$): C, 49.13; H, 3.67. Found: C, 49.0; H, 3.70.

Results

Figure 1 summarizes the preparative conditions and relative yields for the various compounds. It is important to note that the boiling points of octane (125°) and hexane (69°) differ appreciably, and we have not investigated reactions carried out at any intermediate temperatures. It is possible that still other compounds might be found and also that there might be conditions giving improved yields of some of the compounds. However, as noted in the introductory section, the objective in undertaking this research was primarily to obtain analogs of the various COT derivatives of the iron carbonyls and to characterize them structurally and physically, especially in regard to fluxional behavior where that might be encountered. Thus, improvement or extension of the preparative work beyond the requirements imposed by that objective was not attempted. Moreover, the labor required to prepare the TMCOT was such as to discourage its use beyond the minimum quantities required to achieve this objective.

In this section the physical and structural data for each of the five compounds will be presented and, as far as possible, interpreted in regard to molecular structure.

The Structure of Compound I, $(C_{12}H_{16})Fe(CO)_3$. It was hoped that this compound would be the tetramethyl analog of $C_8H_8Fe(CO)_3$ and would, therefore, exhibit fluxional behavior that might help elucidate the $C_8H_8Fe(CO)_3$ problem. However, this molecule has no fluxional behavior which is evident in the nmr spectrum at room temperature, and all the evidence concerning its structure, which will now be discussed, indicates that it contains coordinated 1,3,5,7-tetramethyl-

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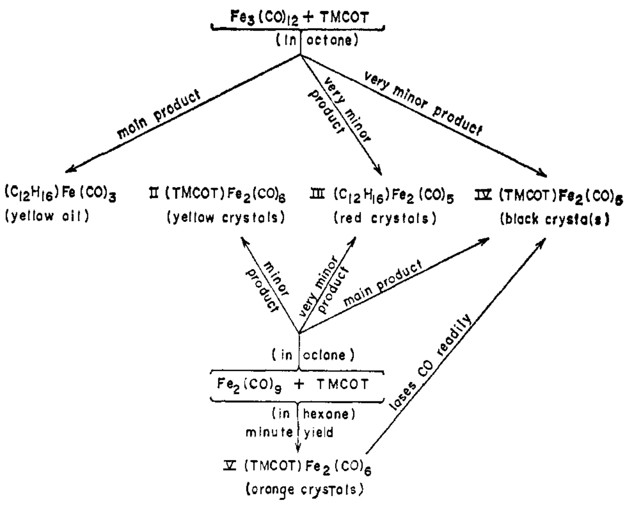


Figure 1. A diagram summarizing the preparative conditions and relative yields of the several compounds.

bicyclo[4.2.0]octa-2,4,7-triene, a molecule which we shall hereafter refer to as "the bicyclic olefin."

That the tetramethyl compound is basically different from $C_8H_8Fe(CO)_3$ is suggested by some striking differences in their properties. (1) The tetramethyl compound is a yellow oil, while $C_8H_8Fe(CO)_3$ is a red, crystalline solid, mp 94°. (2) The uv spectrum of the tetramethyl compound (Figure 2), which has maxima at 235 and ~295 mμ, is similar to the uv spectra of other (1,3-diene)$Fe(CO)_3$ compounds (*e.g.*, the bicyclo[4.2.0]-octa-2,4-diene complex, discussed further below, has maxima at 226 and 284 mμ) but quite different from that of $C_8H_8Fe(CO)_3$ as Figure 2 shows. (3) As noted already, the tetramethyl compound shows no evidence of fluxional behavior in its nmr spectrum at room temperature, whereas $C_8H_8Fe(CO)_3$ shows a static spectrum only when the temperature is reduced to about −150°. (4) Finally, the nmr spectrum seen at room temperature is inconsistent with the presence of either a 1,3- or a 1,5-bonded monocyclic ring but can, as will next be shown, be assigned to a bonded bicyclic [4.2.0] olefin.

There are indirect reasons for considering the bicyclic olefin as a plausible possibility. The bicyclic [4.2.0] isomer of COT itself has been postulated as a reaction intermediate[19] and has actually been isolated in up to 95% purity at −76° though it rapidly isomerizes to the monocyclic isomer.[20] Moreover, methyl groups may have a stabilizing influence on the bicyclic structure since the octamethyl compound, $(CH_3)_8C_8$, is more stable in the bicyclic than in the monocyclic form.[21]

The best direct evidence for the presence of the bicyclic olefin in $(CH_3)_4C_8H_4Fe(CO)_3$ comes from its nmr spectrum, especially when this is compared with similar data for $C_8H_{10}Fe(CO)_3$, which is the iron tricarbonyl complex of bicyclo[4.2.0]octa-2,4-diene.[22] The two structures are shown schematically and their assigned nmr spectra tabulated in Table I.

The infrared spectrum of $(CH_3)_4C_8H_4Fe(CO)_3$ provides no conclusive evidence regarding the bicyclo structure but is consistent with it. Interpretation is hampered by the presence of olefin impurities. Repeated attempts to purify the compound beyond ~97% were unsuccessful, and nmr spectra always showed at least trace quantities of unidentified impurities as well as some 1,3,5,7-tetramethylcyclooctatetraene. This is not particularly unusual with (1,3-diene)$Fe(CO)_3$ compounds, a notable example being the isoprene complex.[23] A complex of the bicyclic olefin would be expected[24,25] to exhibit a C–H stretching band above

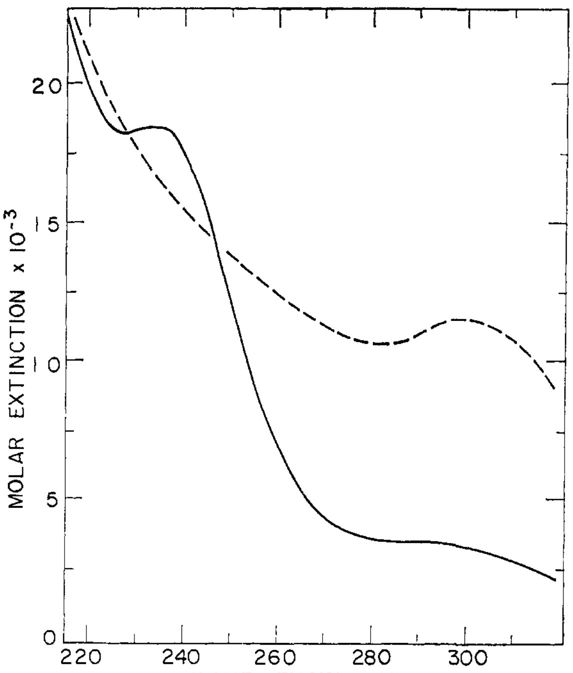
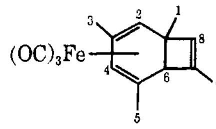
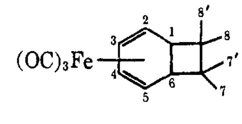


Figure 2. The ultraviolet spectra of $(COT)Fe(CO)_3$ (----) and $(C_{12}H_{16})Fe(CO)_3$ (——) recorded on 4 × 10^{-5} *M* solutions in hexane.

Table I. Nmr Spectra and Assignments[a] for $(CH_3)_4C_8H_4Fe(CO)_3$ and $C_8H_{10}Fe(CO)_3$





τ	Rel intensity	Assignment	τ	Rel intensity	Assignment
4.24	(1)	8			
4.78	(1)	4	4.64	(2)	3,4
7.23	(1)	2	6.63	(2)	2,5
7.70	(1)	6	7.45	(2)	1,6
			8.16 8.83	(4)	7,8
7.97 8.47 8.77	(3) (6) (3)	1,3, 5,7			

[a] Data and assignments for $C_8H_{10}Fe(CO)_3$ from Burton, Pratt, and Wilkinson.[22]

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3000 cm^{-1} and a very weak double bond stretch in the vicinity of 1560 cm^{-1}. The compound does show a medium band at 3031 cm^{-1} and a very weak band at 1570 cm^{-1}. It also has bands at 1480 (weak) and 1402 (medium) cm^{-1} which can be assigned to vibrations of the coordinated double bonds.

Compound II, (TMCOT)Fe$_2$(CO)$_6$. The nmr spectrum of this compound at 25° in carbon disulfide consists of two peaks of relative intensity 1 at τ 4.85 and 7.15 and two peaks of relative intensity 3 at τ 7.76 and 8.29. The infrared spectrum in the CO stretching region contains three bands of practically equal intensities at 2040, 1988, and 1980 cm^{-1} (all ± 5 cm^{-1}).

Considering (a) the yellow color, (b) the stability, (c) the number and positions of the nmr bands, and (d) the infrared bands, we conclude that this compound has the structure II. It is thus the analog of the (COT)-Fe$_2$(CO)$_6$ first reported by Manuel and Stone.[4a] The structure was later determined by Dickens and Lipscomb,[12] and the nmr spectrum has been reported by Keller, Emerson, and Pettit.[9] A well-resolved CO stretching spectrum has not been reported for (COT)-Fe$_2$(CO)$_6$, but it is now well known that under good resolution (butadiene)Fe(CO)$_3$ groups give rise to exactly the sort of three-band spectrum reported here. A three-band spectrum of the same kind would be expected for a dinuclear compound with the structure II.

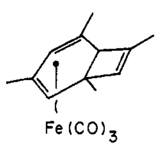
Compound III, (C$_{12}$H$_{16}$)Fe$_2$(CO)$_5$. As noted in the Experimental Section, this compound was obtained only in minute yields—literally only a few small crystals each time. Consequently, definitive physical data were difficult to obtain. It was not possible to record an nmr spectrum with a high enough signal-to-noise ratio to permit unequivocal observation of any signals in the vinyl region. The only definite bands were seen at τ values of about 7.60, 8.05, 8.15, 8.28, and 8.50. For a TMCOT derivative, only the methyl groups would be expected to absorb in this region, so that the appearance of more than four absorptions becomes puzzling.

The infrared spectrum in the CO stretching region contains four resolved bands in the terminal region (2030, (s), 1980 (s), 1970 (s), 1940 (m) cm^{-1}) and no absorption in the region for bridging carbonyl groups.

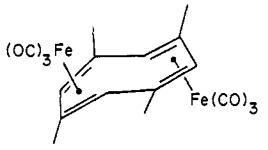
On the basis of the foregoing evidence we were unable to come to any conclusion about the structure of this compound. It was subsequently found by a single-crystal, X-ray study[16] that it contains a coordinated 1,3,5-trimethyl-7-methylenecycloocta-1,3,5-triene molecule, attached to an Fe(CO)$_2$ group and an Fe(CO)$_3$ group which are, in turn, connected to each other by an Fe–Fe bond. The structure is indicated schematically by III; details are given elsewhere.[16] On the basis of this structure the low yields at 125° and zero yield at 69° may be explained because of the rearrangement required. The complex nmr spectrum is also understandable though no assignment of it can be made. The structure would have, in principle, five ir-active CO stretching modes; the observation of only four is most likely due to the accidental degeneracy of a mode localized in the Fe(CO)$_2$ moiety with one localized in the Fe(CO)$_3$ moiety.

Compound IV, (TMCOT)Fe$_2$(CO)$_5$. This compound was isolated from the reactions of both Fe$_2$(CO)$_9$ and Fe$_3$(CO)$_{12}$ with TMCOT in hexane, and with the former it is the major product. The nmr spectrum at 25° consists of only one peak in the vinyl region at τ 5.69 and one peak, three times as intense as the vinyl peak, at τ 7.90. This spectrum is not significantly different at −60°. Thus, compound IV appears to be a fluxional molecule, executing some kind of intramolecular rearrangement rapidly, even at −60°, which permutes all vinyl hydrogen atoms and all methyl groups. It is notably reminiscent in all its properties, including its black color, of Keller, Emerson, and Pettit's[9] (COT)-Fe$_2$(CO)$_5$, for which Fleischer, *et al.*,[11] have found structure IVa. Consequently, we considered the possibility of our compound having an analogous structure, which might be either IVb or IVc.

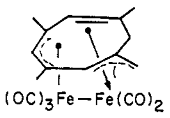
The infrared spectrum of the compound in heptane in the CO stretching region is in good accord with either IVb or IVc. It consists of three bands (2028, 1995, 1959 cm^{-1}, all ± 5 cm^{-1}) in the terminal CO region and one band at 1803 $\pm$ 5 cm^{-1} in the bridging region. Both of the structures IVb and IVc have C_{2v} molecular symmetry. A set of four identical oscillators, equivalent under the operations of the group C_{2v}, will give rise to four normal modes of vibration, one corresponding to each of the irreducible representations A_1, A_2, B_1, and B_2 of the group. Of these, A_2 has no infrared activity, leaving three expected bands plus the (A_1) bridge band, in accord with observation.



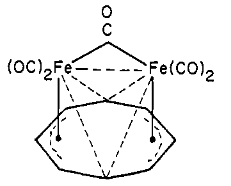
I



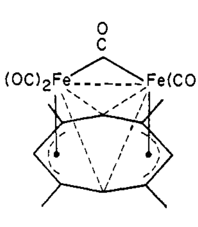
II



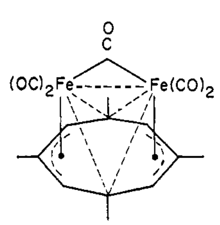
III



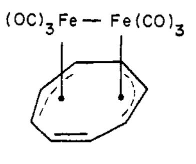
IVa



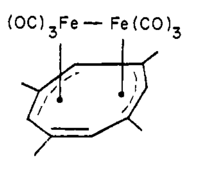
IVb



IVc



Va



Vb

It has been shown in a single-crystal, X-ray study reported elsewhere[15] that IVb is the correct structure of compound IV.

Compound V, (TMCOT)$Fe_2(CO)_6$. This compound has been obtained only by treating $Fe_2(CO)_9$ with TMCOT at low temperature, and then only in minute yields. It is unstable, readily losing CO to give compound IV. In this respect it resembles the compound of Keller, Emerson, and Pettit,[9] for which they proposed structure Va. That it is, definitely, homologous to the Keller, Emerson, and Pettit compound is shown by its nmr and infrared spectra, in conjunction with those of the ruthenium compound (COT)$Ru_2(CO)_6$ which has been extensively studied in this laboratory[17] and shown conclusively to be analogous to (COT)$Fe_2(CO)_6$, the compound formulated as Va.

The nmr spectra of the two COT compounds, (COT)$Fe_2(CO)_6$[9] and (COT)$Ru_2(CO)_6$, are essentially identical[17a] and leave no doubt that these two compounds are isostructural in solution.[26] The infrared spectra of (COT)$Ru_2(CO)_6$ and (TMCOT)$Fe_2(CO)_6$ in the CO stretching region are practically superposable. Also, in accord with the nmr results for the two COT compounds the nmr spectrum (in $CDCl_3$) of compound V has four absorptions, each of relative intensity 1, at τ values of 4.68, 5.03, 5.84, and 6.20, and four, each of relative intensity 3, at τ values of 7.83, 8.11, 8.32, and 8.39 (close doublet).

The infrared spectrum of compound V in the CO stretching region contains five resolved bands in the terminal CO region [2043 (s), 2002 (s), 1974 (s), 1965 (m), and 1947 (m) cm^{-1}, each ± 5 cm^{-1}] and no absorption in the bridging CO region. Any structure of the type Vb would in principle have six ir-active terminal CO stretches, but the accidental superposition of two of them or the absence of one due to low intensity would not be surprising.

The isolation of only compound V in the low-temperature reaction and its absence among the isolated products of the high-temperature reaction are understandable facts. The ready conversion of V to IV by loss of CO explains the absence of V (and the presence of IV) in the high-temperature reaction. Since compounds II and III are obtained only in very small quantities in the high-temperature reaction of TMCOT with $Fe_2(CO)_9$, their absence in the low-temperature reaction is not surprising.

Discussion

It is evident that while TMCOT interacts with $Fe_n(CO)_c$ moieties in some ways which are quite analogous to the behavior of COT, *viz.*, in compounds II, IV, and V, it also exhibits interesting differences. The failure to isolate any TMCOT analog of $(C_8H_8)Fe(CO)_3$, or to obtain any indication at all of its existence, is somewhat surprising and disappointing in view of the objectives of this study. A result of this kind does not appear predictable at our present purely qualitative level of comprehension of metal–olefin bonding.

The formation of compound III, albeit in very minute quantities, is also surprising and was certainly not anticipated. It may well serve as a warning that rearrangements of methyl-substituted olefins by hydrogen shift must not be overlooked in other cases.

The recurrence of compound IV, with its fluxional nature and unusual structure, is noteworthy. It is certainly not clear why structure IVb rather than IVc is preferred, nor even why this kind of structure, in either form, is adopted. Further discussion of it will be given in the report[15] on the crystallographic study of compound IV.

Finally, we note that no indication was obtained in this work of still another (TMCOT)$Fe_2(CO)_6$ tautomer, besides II and V, as in the case[9] of (COT)$Fe_2(CO)_6$.

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(26) Note Added in Proof. The discussion here was written before an X-ray study[17a,c] had shown that $C_8H_8Ru_2(CO)_6$ does *not* have a structure of the type Va in the crystal and should be treated accordingly. Structure Vb is thus, presumably, irrelevant. Efforts by Mrs. M. D. La Prade to determine the crystal structure of compound V were unsuccessful owing to the inherent instability of the substance and the limited quantities available.