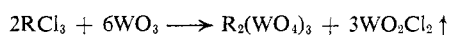


To prevent a severe change of the melt composition because of the continuous loss of WO_3 , the crystals were grown relatively quickly from large quantities of fused earth tungstate and tungsten trioxide. It appears that the current density has to be increased when the temperature of the melt is increased. Best results were obtained by electrolyzing appropriate mixtures of tungsten trioxide and rare earth tungstate around 1200° using current densities up to 60 ma/cm^2 . The crystals were grown in the thermoconstant portion of a tubular furnace which was continuously flushed with argon. The electrodes were made of platinum which was observed to have more favorable properties than nichrome, tungsten, or carbon. Recrystallized alumina (no platinum!) served as crucible material. Both single cell and double cell assemblies were used.

Instead of melting the mixture of rare earth tungstate and tungsten trioxide directly, it was found to be more advantageous to melt a mixture of rare earth chloride and tungsten trioxide.⁶ The following reaction takes place



Very homogeneous melts were obtained this way. The electrolysis was usually started after the WO_2Cl_2 liberation was terminated.

Crystals grown in the course of this investigation had the composition $\text{Sm}_{0.09}\text{WO}_3$, $\text{Gd}_{0.19}\text{WO}_3$, and $\text{Tm}_{0.10}\text{WO}_3$. $\text{Sm}_{0.09}\text{WO}_3$ crystals up to 5 mm in length were obtained within 20 min at 1300° using a mixture of SmCl_3 and WO_3 (molar ratio 1:3). The $\text{Gd}_{0.19}\text{WO}_3$ crystals, up to 10 mm in length, were grown from a molten mixture of GdCl_3 and WO_3 (molar ratio 1:2) 20° above the melting point of the mixture. It may be mentioned that the gadolinium content of the $\text{Gd}_{0.19}\text{WO}_3$ crystals is somewhat higher than that of the gadolinium richest samples obtained in the form of powders by thermal reaction of Gd_2O_3 , W, and WO_3 .¹

All single crystals prepared in the course of this investigation were examined by X-ray diffraction methods and analyzed for their rare earth content by magnetic susceptibility measurements.

Acknowledgments. The authors wish to thank Professor Aaron Wold of Brown University and Dr. H. Shanks of the Institute of Atomic Research, Ames Laboratory, for many stimulating discussions.

(6) L. E. Conroy and P. Yokokawa (*Inorg. Chem.*, **4**, 94 (1965)) have reported a similar method for the preparation of barium tungsten bronzes.

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Trimethylenemethaneiron Tricarbonyl

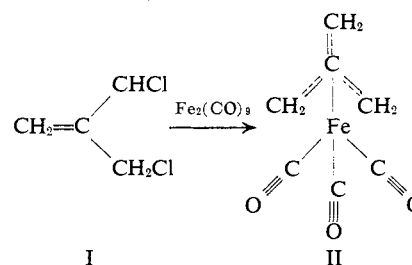
Sir:

In many instances it has been possible to obtain transition metal π complexes containing as ligands organic molecules which in the free state are sufficiently reactive or subject to internal rearrangement to preclude their isolation under normal conditions. Some examples are the iron carbonyl complexes of cyclobutadiene,¹

(1) G. F. Emerson, L. Watts, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 131 (1965).

benzocyclobutadiene,¹ cyclopentadienone,² and 2,4-cyclohexadienone.³ We now report the isolation of a metal complex containing the organic fragment trimethylenemethane as a ligand. This hypothetical molecule has long been of theoretical interest in that it displays at its central carbon the maximum mobile bond order and minimum free valence possible for an unsaturated hydrocarbon system.⁴ Its bonding to transition metals may be anticipated. Since trimethylenemethane would possess an extremely unfavorable delocalization energy, little π energy will be dissipated in donation to a metal,⁵ and since theoretical treatments suggest that there is an unfilled nonbonding orbital, as with cyclobutadiene, it should also be an excellent acceptor in transition metal complexes.⁶

Excess iron enneacarbonyl was stirred with 3-chloro-(2-chloromethyl)propene (I)⁷ in ether at room temperature for 12 hr; the mixture was then filtered and fractionally distilled. The pale yellow complex trimethylenemethaneiron tricarbonyl (II) was obtained in 30% yield, bp $53\text{--}55^\circ$ (16 mm), mp $28.4\text{--}29.6^\circ$, n_D^{20} 1.5879. *Anal.* Calcd for $\text{C}_4\text{H}_6\text{Fe}(\text{CO})_3$: C, 43.31; H, 3.12. Found: C, 43.29; H, 2.90. In the mass spectrum of II strong peaks corresponding to the parent molecular ion and fragments resulting from the successive loss of one, two, and three carbonyl groups are observed at m/e 194, 166, 138, and 110. This type of cracking pattern is observed with cyclobutadieneiron tricarbonyl¹ and many derivatives.⁸



The infrared spectrum of the complex shows strong carbonyl absorption at 1998 and 2064 cm^{-1} , typical of symmetrical diene- $\text{Fe}(\text{CO})_3$ complexes.^{9,10} Other bands appear at 3067 (m), 3000 (m), 2885 (w), 2475 (w), 1805 (w), 1566 (w), 1478 (m), 1456 (m), 1349 (w), 1025 (w), 917 (m), and 803 cm^{-1} (m). The nmr spectrum shows a sharp singlet at τ 8.00 indicating the equivalency of all hydrogens.¹¹ This shift may be compared to those in the spectrum of the isomeric butadieneiron tricarbonyl in which the proton signals of the terminal positions appear at τ 8.32 (*syn*) and 9.78 (*anti*);^{9,12} to the

(2) (a) M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 989 (1960); (b) E. Weiss, R. Merényi, and W. Hübel, *Chem. Ind.* (London), 407 (1960).

(3) A. J. Birch, P. E. Cross, J. Lewis, and D. A. White, *ibid.*, 838 (1964).

(4) J. D. Roberts, "Notes on Molecular Orbital Calculations," W. A. Benjamin, Co., New York, N. Y., 1962, pp 56, 58, 128.

(5) The ability of unsaturated hydrocarbons to form diene-iron carbonyl complexes has been correlated with the expected loss of delocalization energy attendant on complexation: B. J. Nicholson, private correspondence.

(6) H. C. Longuet-Higgins and L. E. Orgel, *J. Chem. Soc.*, 1969 (1956).

(7) B. C. Anderson, *J. Org. Chem.*, **27**, 2720 (1962).

(8) J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

(9) R. Pettit and G. F. Emerson, *Advan. Organometal. Chem.*, **1**, 1 (1964).

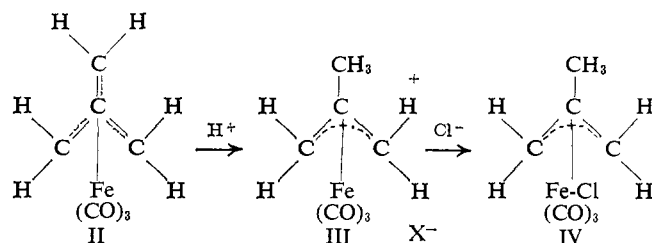
(10) R. Pettit, G. F. Emerson, and J. E. Mahler, *J. Chem. Educ.*, **40**, 175 (1963).

(11) The line width at half-height was found to be 0.6 cps. Measurements were taken on a Varian A-60.

methylene proton peaks of π -allyl- π -cyclopentadienyl-iron monocarbonyl seen at τ 7.33 (*syn*) and 9.32 (*anti*);¹² and to the band at τ 6.09 of cyclobutadiene-iron tricarbonyl.¹

The C^{13} spectrum¹³ of II consists of a singlet at -18.8 ± 1.0 ppm ($CS_2 = 0$), another singlet at $+87.8 \pm 1.0$ ppm, and a triplet at $+139.8 \pm 1.0$ ppm with a splitting of 158 ± 10 cps. From the C^{13} satellites in the proton spectrum, each appearing as a doublet with a splitting of 5 cps, $J_{C,H} = 162 \pm 1$ cps; this coupling value is typical for olefin π complexes.^{14,15} The low-field C^{13} singlet is at a position typical for metal carbonyls,¹⁴ while the triplet appears at a value intermediate to those of the carbons of butadieneiron tricarbonyl and slightly higher than that of cyclobutadieneiron tricarbonyl.¹⁵ Although the central carbon falls at an unusually low position for a π complex, the difference in shift (52 ppm) between it and the methylene carbons is rather less than would be theoretically predicted¹⁶ for the free molecule (64 ppm) and far less than would be predicted from an empirical comparison with allene.¹⁷ This suggests that the central carbon signal may be furthest shifted upfield, reflecting a stronger interaction with the metal.^{14,15}

In view of the extraordinarily facile valence tautomerism seen in some iron carbonyl complexes,¹⁸ structures other than the symmetrical one in which the iron atom is situated directly below the central carbon may be considered. The compound would then be observed as the symmetrical average of three rapidly equilibrating asymmetric structures. In one conceivable set of structures the $Fe(CO)_3$ grouping might be bonded only to an allyl portion of the ligand, in another set to the double bond of methylenecyclopropane. In both cases, however, the inert gas configuration of iron would be violated; and in the first case the average of the nmr signals might be expected at lower field than is found, while the second possibility requires the twisting of methylene groups in and out of plane and the rapid formation and cleavage of carbon-carbon bonds. No broadening of the proton signal was observed at -60° .¹⁹



Protonation of the ligand occurs in strong acids, as with butadieneiron tricarbonyl and derivatives;²⁰ a

(12) M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organometal. Chem.*, **3**, 1 (1965).

(13) Measurements were taken at 25.143 Mc.

(14) P. C. Lauterbur and R. B. King, *J. Am. Chem. Soc.*, **87**, 3266 (1965).

(15) H. G. Preston and J. C. Davis, *ibid.*, **88**, 1585 (1966).

(16) (a) M. Karplus and J. A. Pople, *J. Chem. Phys.*, **38**, 2803 (1963);

(b) J. A. Pople, *Mol. Phys.*, **7**, 301 (1964).

(17) R. A. Friedel and H. L. Retcofsky, *J. Am. Chem. Soc.*, **85**, 1300 (1963).

(18) C. E. Keller, G. F. Emerson, and R. Pettit, *ibid.*, **87**, 1388 (1965).

(19) That the complex II has a higher melting point and narrower liquid range than either cyclobutadieneiron tricarbonyl or butadieneiron tricarbonyl might be taken to indicate higher symmetry.

(20) G. F. Emerson and R. Pettit, *J. Am. Chem. Soc.*, **84**, 4591 (1962).

solution of the complex II in 96% H_2SO_4 exhibits an nmr spectrum nearly identical with that of π -2-methylallyliron tricarbonyl perchlorate (III),^{21,22} with three singlets at τ 8.0, 7.3, and 5.0, the relative intensities being 3:2:2. Treatment of the complex II with H_2SO_4 , followed by concentrated HCl, gave rise to the known covalent chloride (IV)^{21,22} in high yield; the nmr spectrum of IV consists of three singlets at τ 8.01, 6.73, and 5.68.

Further investigations of this and related systems are presently underway.

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(21) G. F. Emerson, Dissertation, University of Texas, 1964.

(22) G. F. Emerson, J. E. Mahler, and R. Pettit, *Chem. Ind. (London)*, 836 (1964).

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Isindole Formation by a Novel Rearrangement

Sir:

We have found that 1-alkyl-substituted 2,3-dihydro-5-phenyl-(1H)-1,4-benzodiazepin-2-ones of type I readily undergo rearrangement to give N-alkyl-3-phenyl-1-isindolecarboxamides of type IV, mp 218–220°, $\nu_{NH}^{CHCl_3}$ 3420 and 3480 cm^{-1} ; $\nu_{C=O}^{CHCl_3}$ 1630 and 1540 cm^{-1} ; nmr spectrum (DMF- d_7) $NHCH_3$, three-proton doublet centered at δ 3.01 ($J = 5$ cps); λ_{max} (2-propanol) 221 (ϵ 14,600), 230 (ϵ 15,200), 258 (ϵ 33,000), 295 (ϵ 5900), and 369 $m\mu$ (ϵ 22,500). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 76.88; H, 5.99. This rearrangement was carried out at about 60° in N,N-dimethylformamide solution with 1 equiv of sodium hydride. The yield of isolated product was $>80\%$. Unlike most isindoles, these compounds are extremely stable and easy to purify. This is probably due to the resonance stabilization imparted to the molecule by the carboxamido function.

There has been much discussion as to whether or not isindole is more stable than the tautomeric isindolenine.¹ Lwowski was able to show by nmr studies that, in solution, 1-phenylisindoles are in equilibrium with the tautomeric isindolenines,¹ while Bender and Bonnett have recently reported that 1,3,4,7-tetramethylisindole exists mainly as the isindolenine tautomer.² For the first time, we have been able to isolate both possible tautomers of an isindole. By treating a solution of IV in N,N-dimethylformamide with sodium carbonate we obtained the isindolenine III,³ mp

(1) See D. F. Veber and W. Lwowski, *J. Am. Chem. Soc.*, **86**, 4152 (1964), and references cited therein.

(2) C. O. Bender and R. Bonnett, *Chem. Commun.*, 198 (1966).

(3) Structure III is preferred to the other possible isindolenine structure on the basis of the shift in the frequency of the carbonyl absorption in the infrared spectrum and the chemical shift of the methyl group in the nmr spectrum when compared to the corresponding spectra for com-