The value of the second-order specific rate for formation of the N_2O complex may be compared with the formation rates of other $(NH_3)_5Ru^{II}L^{2+}$ complexes at 25°. For $L = N_2$, $(NH_3)_5RuN_2^{2+}$, N_2O, CO, pyridine, and isonicotinamide, $k = 7.1 \times 10^{-2}$,[6] 4.2×10^{-2},[6] 7.21×10^{-2}, 12×10^{-2},[9] 11.8×10^{-2},[10] and 6×10^{-2} M^{-1} sec^{-1}.[11]

Acknowledgment. Financial support by the National Institutes of Health, Grant No. GM 13638-03, and the National Science Foundation, Grant No. GP 5322, is gratefully acknowledged.

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(9) D. F. Harrison, Ph.D. Thesis, Stanford University, Stanford, Calif., Jan 1969.

(10) A. R. Allen, R. Hintze, and P. C. Ford, to be submitted for publication.

(11) J. N. Armor, unpublished result.

John N. Armor, H. Taube
Department of Chemistry, Stanford University
Stanford, California 94305
Received August 23, 1969

Synthesis of Cyclooctatetraenyleuropium and Cyclooctatetraenylytterbium

Sir:

The preparation of bis(cyclooctatetraenyl)uranium(IV),[1] which has received the trivial name "uranocene," has renewed interest in new types of compounds containing cyclooctatetraene. Aside from uranocene, compounds of formula $M(Cot)_2$, with M = V, Ti, have been known for some time. Several compounds of formula M(Cot) are also known,[2] as is one mixed cyclopentadienyl–cyclooctatetraenyl compound, Co(cp)(Cot),[3] and many Cot–carbonyl compounds. We report here the preparations and some properties of cyclooctatetraene compounds of Yb and Eu. We believe these to be the first reported cyclooctatetraene complexes of rare earth elements.

It is well known that solutions of ytterbium and europium in liquid ammonia may be used to prepare the respective cyclopentadienides.[4] The cyclooctatetraene derivatives of these elements were successfully synthesized using similar techniques. Because of the almost explosive air oxidation of both compounds, all studies were carried out under anaerobic conditions. Also, in contrast to $U(Cot)_2$,[1] both compounds undergo immediate hydrolysis in the presence of water.

One would expect to obtain compounds of the type M(Cot) from Yb and Eu, since these elements both have stable +2 oxidation states. This expectation is fulfilled. Analysis of the Yb compound substantiates the formulation Yb(Cot). The Yb compound is, furthermore, diamagnetic. The Eu compound has an epr spectrum visible at 77°K, which is consistent only with Eu^{2+}. The epr spectrum of the powdered compound consists of a strong resonance 4 kG wide, peak-to-peak, centered on $g = 2.00$.

The compounds appear to have strong interactions with solvents, which affect their appearance markedly. The unsolvated Yb compound is, for example, pink. It is insoluble in ammonia, but becomes orange. Removal of excess ammonia at atmospheric pressure yields a compound which is a very intense blue. Removal of ammonia under vacuum yields the original compounds. Yb(Cot) is insoluble in hydrocarbons and ethers but dissolves in more basic solvents, such as pyridine and dimethylformamide. The solutions are deep red and the solids in contact with them are nearly black. These solvents may be removed under vacuum.

Both compounds are stable to 500° under vacuum. Neither sublimes at 500° and 10 μ.

There is no marked difference between the epr spectra of unsolvated Eu(Cot) and the compound solvated with NH_3. This means only that there has been no remarkable change in the electrical asymmetry of the environment of the Eu^{2+} in the two cases.

The compounds were prepared by the dropwise addition of cyclooctatetraene to ytterbium or europium metal dissolved in anhydrous ammonia. The reactions were carried out under a purified nitrogen atmosphere. In a typical reaction, 0.01 mole of cyclooctatetraene was added slowly to 0.01 mole of the metal, yielding an orange or light green precipitate for ytterbium or europium, respectively. After stirring for 2 hr, the remaining ammonia was removed and a bright blue or light green product recovered. Upon heating to 200° at 10^{-3} mm, a pink (Yb) or orange (Eu) product was obtained. Carbon and hydrogen analyses were slightly off, but consistent with a 1:1 complex. *Anal.* Calcd: C, 34.7; H, 2.9. Found: C, 30.5; H, 3.0. Metal analysis, carried out in the same manner as that for ytterbium cyclopentadienide,[5] gave excellent agreement for a 1:1 complex. *Anal.* Calcd for Yb(Cot): Yb, 62.4. Found: Yb, 62.1. Analysis of the pink Yb(Cot) indicated that less than 0.5% nitrogen was present. All solvents used were purified by refluxing over calcium hydride or by contact with potassium mirrors. Electron paramagnetic resonance measurements were performed on a Varian V-4502-15 X-band spectrometer, and magnetic susceptibilities were determined with a simple Gouy balance using $HgCo(NCS)_4$ as a standard.

Acknowledgment. The partial support of this work by National Science Foundation Grant No. 7881 is gratefully acknowledged.

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(1) A. Streitwieser, Jr., and U. Müller-Westerhoff, *J. Am. Chem. Soc.*, **90**, 7364 (1968).

(2) H. Breil and G. Wilke, *Angew. Chem. Intern. Ed. Engl.*, **5**, 898 (1966).

(3) A. Nakamura and N. Hagihara, *Bull. Chem. Soc. Jap.*, **33**, 425 (1960).

(4) E. O. Fischer and H. Fischer, *J. Organometal. Chem.*, **3**, 181 (1965).

(5) J. M. Birmingham and G. Wilkinson, *J. Am. Chem. Soc.*, **78**, 42 (1956).

Robert G. Hayes, Joseph L. Thomas
Department of Chemistry, University of Notre Dame
Notre Dame, Indiana
Received August 4, 1969

Fluxional Behavior of (*Trihapto*cycloheptatrienyl)-(*pentahapto*cyclopentadienyl)monocarbonyliron

Sir:

We recently reported the preparation of a substance which was assigned the structure of a 7-*monohapto*cycloheptatrieneiron complex.[1] Further examination of this substance and a comparison of its nmr spectrum

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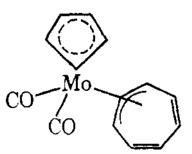
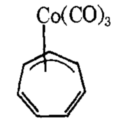
(1) D. Ciappenelli and M. Rosenblum, *J. Am. Chem. Soc.*, **91**, 3673 (1969).

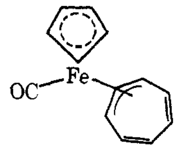
with that of (*trihapto*cycloheptatrienyl)(*pentahapto*cyclopentadienyl)dicarbonylmolybdenum[2,3] (**1**) and of (*trihapto*cycloheptatrienyl)tricarbonylcobalt[3] (**2**) require that it be reformulated as the *trihapto*cycloheptatrienyl complex **3**.



1



2



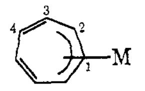
3

The infrared spectrum of **3**, taken in cyclohexane solution, exhibits a single intense carbonyl peak at 1959 cm^{-1} which compares well with carbonyl absorption reported for $(h^5\text{-}C_5H_5)(h^3\text{-}C_3H_5)Fe(CO)$ and $(h^5\text{-}C_5H_5)(h^3\text{-}C_4H_7)Fe(CO)$ of 1950 and 1948 cm^{-1}, respectively.[4] The multiple carbonyl peaks shown by solutions of **3** in carbon tetrachloride solution, reported previously,[1] apparently arise from decomposition of the substance in these solutions.[5]

Although crystalline samples of **3** exhibited a mass spectral peak at *m/e* 268 corresponding to the molecular ion for the complex $(h^5\text{-}C_5H_5)(h^1\text{-}C_7H_7)(CO)_2Fe$, further extensive purification by column chromatography and recrystallization from petroleum ether at low temperatures result in the elimination of this peak. The purified complex exhibits peaks at *m/e* 240 [$(C_5H_5)(C_7H_7)COFe^+$], 212 [$(C_5H_5)(C_7H_7)Fe^+$], 147 ($C_7H_7Fe^+$), 121 ($C_5H_5Fe^+$), 91 ($C_7H_7^+$), and 56 (Fe^+), with metastables at *m/e* 187.3 and 101.9 for the transitions 240 → 212 and 212 → 147.

The close correspondence in the proton resonances for the complexes **1**, **2**, and **3**, which are summarized in Table I, illustrates the close structural relationship of these substances. It seems probable that the anomalous chemical shifts of the h^3-allyl protons, in particular the high-field resonance of the H_1 proton and the deshielding of H_2 protons, are associated with anisotropy effects of the uncomplexed diene portion of the seven-membered ring, as has recently been suggested by Bennett, Bramley, and Watt.[3] The deshielding of H_3 protons may similarly be attributed to a reciprocal effect of the complexed h^3-allyl grouping on these diene protons.[6]

Table I. Proton Resonances[a] in $h^3\text{-}C_7H_7$ Metal Complexes



Compd	δ(H$_1$)	δ(H$_2$)	δ(H$_3$)	δ(H$_4$)	Solvent	Ref
1[b]	2.32	4.59	6.50	5.40	$CHCl_2F$	2
2	3.5	4.85	~6.5	~5.80	CF_2Cl_2	3
3[b]	3.08	4.75	6.10	5.15	$CDCl_3$	This work

[a] In parts per million. [b] Assignment of resonances made by low-temperature double-resonance experiments.

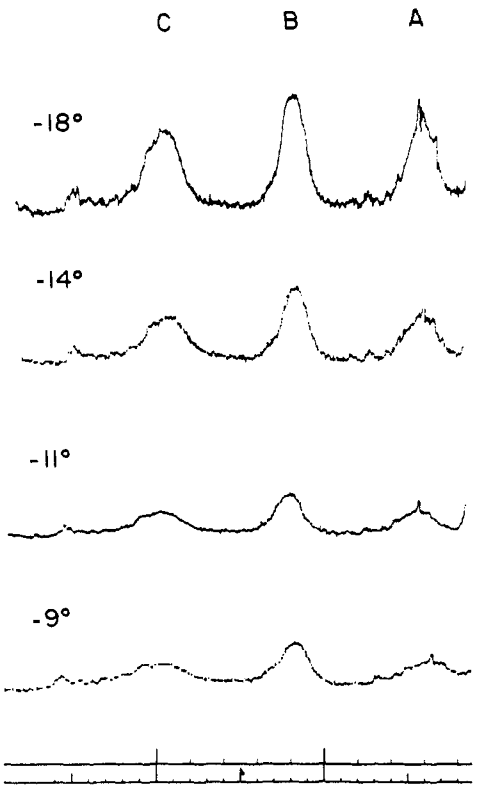


Figure 1. Temperature dependence of the nmr spectrum of $(h^5\text{-}C_5H_5)(h^3\text{-}C_7H_7)Fe(CO)$. Determined in toluene-$d_8$ solution at 100 MHz.

The fluxional behavior of **3** has previously been noted.[1] We now provide evidence that proton averaging in this substance takes place exclusively, or at least predominantly, by a sequence of rapid 1,2 shifts of the metal–carbon bond.

It can readily be shown that for mechanisms of proton averaging in **3** involving successive 1,2, 1,3, or 1,4 shifts of the metal–carbon bond the rate of proton exchange is least for H_4, H_2, and H_3 protons, respectively.[7] The nmr spectra of **3** (Figure 1) show that, in the temperature range of approximately −18 to −9°, in which slow proton exchange occurs, and in which there is little overlap of A, B, and C proton peaks, it is the B proton (H_4) which is broadened significantly less than the A (H_2) and C (H_3) proton signals. Proton exchange must consequently involve a sequence of 1,2 metal–carbon bond hops as the predominant intramolecular motion. This conclusion is further supported by a comparison of the nmr spectral changes, which occur in the region of rapid exchange, with the line-shape functions calculated for each of the averaging processes, employing the method of Kubo[8] and Sack[9] and the computer program of Whitesides and Lisle.[10]

The course of intramolecular rearrangement in **3** is thus the same as that observed in the closely related molybdenum complex **1**[2] and its iron tricarbonyl de-

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[2] J. W. Faller, *Inorg. Chem.*, **8**, 767 (1969).

[3] M. A. Bennett, R. Bramley, and R. Watt, *J. Am. Chem. Soc.*, **91**, 3089 (1969).

[4] M. L. H. Green and P. L. I. Nagy, *J. Chem. Soc.*, 189 (1963).

[5] The decomposition product, which has not been fully characterized, exhibits absorption at 2010 and 2050 cm^{-1} in cyclohexane solution, and is probably $(h^5\text{-}C_5H_5)Fe(CO)_2Cl$; ir (cyclohexane) 2010, 2050 cm^{-1}.

[6] Protons H_1 and H_2 in 1,3-cycloheptadiene show absorption at δ 5.70.

[7] For a random exchange process, one in which the metal may reestablish a bond with equal probability to each of the ring carbon atoms, the rate of proton exchange is identical for all ring protons.

[8] R. Kubo, *Nuovo Cimento Suppl.*, **6**, 1063 (1957).

[9] R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

[10] Program to compute and plot line shapes for exchange-broadened nmr spectra, NMRCTL, 1967. We are indebted to Professor Whitesides for providing us with a copy of this program.

rivative[11] and which has been inferred for the cobalt complex **2**.[3]

Acknowledgment. We are grateful to Professor E. Grunwald for helpful discussions and to Mr. T. Marks of the Massachusetts Institute of Technology for assistance in carrying out the computation. This work was supported by a grant from the National Science Foundation (GP-8714), which is gratefully acknowledged.

(11) F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.*, **91**, 847 (1969).
(12) NDEA Title IV Fellow.

D. Ciappenelli,[12] M. Rosenblum
Department of Chemistry, Brandeis University
Waltham, Massachusetts 02154
Received July 23, 1969

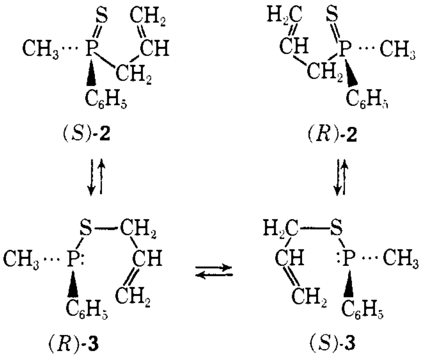
Stereomutation of a Tetracoordinate Phosphorus Compound by Intramolecular Ligand Exchange[1]

Sir:

It has been established that the thermal racemization of allyl sulfoxides proceeds by a concerted, reversible, and intramolecular rearrangement mechanism.[2] We now wish to report the first example of an analogous process in which phosphorus is the chiral center.

Hexachlorodisilane reduction[3] of (+)-(*R*)-allylmethylphenylphosphine oxide (**1**),[4] followed by treatment of the resulting phosphine with elemental sulfur, gave (−)-(*S*)-allylmethylphenylphosphine sulfide (**2**),[5] which was found to racemize in *o*-xylene with first-order kinetics: $k_{\mathrm{rac}} \times 10^6$ (sec^{-1}) = 3.53 (at 205°), 8.92 (at 215°), 10.4 (at 221°), and 14.7 (at 225°), whence E_a = 33 ± 2 kcal/mol and log A = 9.6 ($\Delta S^{\ddagger}$ −18 eu).

Scheme I



According to the racemization route depicted in Scheme I, (*S*)-**2** undergoes a [2,3] sigmatropic rearrangement[6] to allyl (*R*)-methylphenylthiophosphinite (**3**), which is converted to (*S*)-**3** by pyramidal inversion at phosphorus. Allylic rearrangement of (*S*)-**3** to (*R*)-**2** completes the conversion of (*S*)-**2** into its enantiomer.[7]

The rearrangement step is reversible: allyl diphenylthiophosphinite rearranges to allyldiphenylphosphine sulfide.[8] That the rearrangement is concerted was demonstrated by the observation that crotyl diphenylthiophosphinite and α-methylallyl diphenylthiophosphinite readily and completely (>95%) rearrange to α-methylallyldiphenylphosphine sulfide and crotyldiphenylphosphine sulfide, respectively.[9] The rearrangement of racemic **3**[10] in 1,2-$C_6H_4(CD_3)_2$ is also complete (>99%) and follows first-order kinetics:[11] $k \times 10^4$ (sec^{-1}) = 0.48 (at 21°), 1.27 (at 30°), and 5.18 (at 42°), whence E_a = 20 kcal/mol and log A = 10.8 ($\Delta S^{\ddagger}$ −11 eu). The negative entropy of activation attests to the cyclic character of the transition state in the rearrangement of **3** to **2**. It is interesting to note that the rearrangement of allyl thiophosphinites such as **3** is considerably more facile than that of the analogous allyl phosphinites.[4]

The proposed mechanism for racemization of **2** is completely analogous to that of the racemization of allyl sulfoxides,[2] the chief difference residing in the nature of the conformational interconversions which take place at the intermediate stage; whereas both torsion and pyramidal inversion are required to interconvert enantiomeric thiophosphinites,[12] torsion alone (about single bonds) suffices to interconvert enantiomeric conformers of sulfenates. Racemization in either system may thus be viewed as an intramolecular ligand exchange which proceeds in two discrete steps: a rearrangement step, in which bonds are made and broken in a concerted [2,3] sigmatropic process, and the racemization step proper, a conformational change in which bonds are neither made nor broken.

Extensions of the processes herein described to those in isoelectronic phosphorus-containing systems are readily envisaged.[15]

(1) We are grateful to the Air Force Office of Scientific Research for support of this research under Grant No. AF-AFOSR-1188-B.

(2) D. R. Rayner, E. G. Miller, P. Bickart, A. J. Gordon, and K. Mislow, *J. Amer. Chem. Soc.*, **88**, 3138 (1966); K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, and K. Mislow, *J. Amer. Chem. Soc.*, 90, 4869 (1968).

(3) K. Naumann, G. Zon, and K. Mislow, *ibid.*, **91**, 2788 (1969).

(4) A. W. Herriott and K. Mislow, *Tetrahedron Lett.*, 3013 (1968).

(5) Experimental details of this preparation are reported elsewhere (G. Zon, K. E. DeBruin, K. Naumann, and K. Mislow, *J. Amer. Chem. Soc.*, in press).

(6) A. Jefferson and F. Scheinmann, *Quart. Rev.* (London), 22, 391 (1968).

(7) It is not known which of the two steps is rate determining.

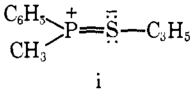
(8) A. E. Arbuzov and K. V. Nikonorov, *Zh. Obshch. Khim.*, **18**, 2008 (1948).

(9) The diphenylthiophosphinites were prepared from crotyl and α-methylallyl thiol by the procedure of Arbuzov and Nikonorov.[8] The sulfides from each rearrangement were >95% homogeneous by pmr ($CDCl_3$), as gauged by the well-separated and characteristic methyl proton resonances. In crotyldiphenylphosphine sulfide these appear at τ 8.26–8.52 (m), whereas in the α-methylallyl isomer the A portion of an A_3BX spin system is centered at τ 8.76, with J_{HCCH} = 7 Hz and J_{HCCP} = 18 Hz.

(10) Prepared from methylphenylbromophosphine and the lithium salt of allyl thiol.

(11) As measured by the rate of attenuation of the methyl doublet (τ 8.63, J_{HCP} = 7.5 Hz) of **3** and the rate of growth of the methyl doublet (τ 8.51, J_{HCP} = 13 Hz) of **2**.

(12) Pyramidal flattening may be facilitated by pπ–dπ overlap of the lone pair of electrons on phosphorus with the 3d orbital of sulfur (see i). Similar effects have been proposed to rationalize facilitated pyramidal inversion in diphosphines[13] and thiolsulfinates.[14] The same factor may also contribute to the ease of racemization of **2**, relative to the corresponding phosphine *oxide*, **1**.[4]



$$\begin{matrix} C_6H_5 \\ CH_3 \end{matrix} \!\!> \overset{+}{P} = \overset{-}{\ddot{S}} - C_3H_5$$

i

(13) J. B. Lambert and D. C. Mueller, *J. Amer. Chem. Soc.*, **88**, 3669 (1966).

(14) P. Koch and A. Fava, *ibid.*, **90**, 3867 (1968).

(15) For example, the racemization of allylic sulfoxides[2] has been discussed in its relation to the rearrangement of sulfonium ylids (J. E. Baldwin, R. E. Hackler, and D. P. Kelly, *Chem. Commun.*, 538 (1968)).

(16) (a) National Science Foundation Trainee, 1968–1969; (b) National Science Foundation Postdoctoral Fellow, 1967–1968.

William B. Farnham,[16a] Arthur W. Herriott,[16b] Kurt Mislow
Department of Chemistry, Princeton University
Princeton, New Jersey 08540
Received August 21, 1969