(and primary) peroxy radicals at room temperature. The relative importance of the alternate mode of reaction, formation of oxygen and two alkoxy radicals which rapidly disproportionate, has still to be determined. It is to be expected that the importance of this reaction mode will depend on the peroxy radical and will increase with increasing temperature.[12] It is perhaps worth pointing out that even exclusive termination by the Russell mechanism does not imply that all peroxy radical self-reactions are chain terminating. The electronically excited ketone (n,π^*) occasionally formed in the termination process[13] is an active hydrogen atom abstracting species[14] quite capable of continuing the chain. However, the efficiency of excitation of the ketone appears to be too low ($\sim 10^{-5}$–10^{-6})[13] to account for the reported 10% excess of cyclohexanol over cyclohexanone found in the products of pulse-radiolyzed cyclohexane saturated with oxygen.[15]

[12] The activation energy for this type of decomposition of tertiary tetroxides is as high as 11–14.5 kcal/mole: P. D. Bartlett and G. Guaraldi, *J. Am. Chem. Soc.*, **89**, 4799(1967); J. R. Thomas and K. U. Ingold, Preprints of the International Oxidation Symposium, Vol. 1, Stanford Research Institute, San Francisco, Calif., 1967, p 517.

[13] R. F. Vasil'ev, *Progr. Reaction Kinetics*, **4**, 305 (1967).

[14] Comparable to a *t*-butoxy radical. See, *e.g.*, C. Walling and M. J. Gibian, *J. Am. Chem. Soc.*, **87**, 3361 (1965).

[15] A. Maclachlan, *ibid.*, **87**, 960 (1965); R. Blackburn and A. Charlesby, *Trans. Faraday Soc.*, **62**, 1159 (1966); W. A. Cramer, *J. Phys. Chem.*, **71**, 1171 (1967); *cf.* however, **71**, 1112 (1967).

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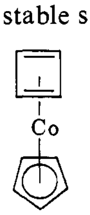
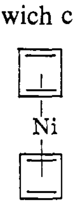
Cyclobutadiene(π-cyclopentadienyl)cobalt

Sir:

The effective atomic number rule provides a useful though not infallible guideline when attempting to predict novel organometallic systems which might possess thermodynamic stability. Thus dibenzenechromium, benzene(π-cyclopentadienyl)manganese, and bis(cyclopentadienyl)iron (ferrocene) all conform to this rule. Extension of this particular series to cobalt and nickel suggests that cyclobutadiene(π-cyclopentadienyl)cobalt (I) and bis(cyclobutadiene)nickel (II) might also exist as stable sandwich complexes.

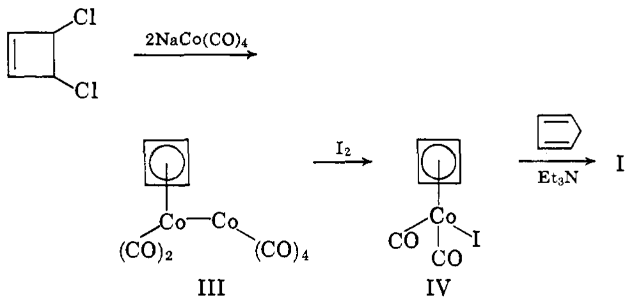


I



II

The tetraphenylcyclobutadiene analog of I and, more recently, the tetramethylcyclobutadiene derivative have been reported.[1,2] We now wish to report the isolation of the parent system I. The key step in the synthesis, the formation of the cyclobutadiene–cobalt bond, employs the reaction between 3,4-dichlorocyclobutene and a metal carbonyl anion; such interactions have recently been found useful for the preparation of other novel cyclobutadiene–metal complexes.[3]



Treatment of 3,4-dichlorocyclobutene with 2 moles[4] of NaCo(CO)$_4$ in tetrahydrofuran produced cyclobutadienedicobalt hexacarbonyl (III) [bright red crystals from pentane,[5] mp 38°; nmr, τ 5.42 (singlet)]. Reaction of complex III with iodine gave cyclobutadienecobalt dicarbonyl iodide (IV) [red crystals, mp 85° dec; nmr, τ 5.32 (singlet)]. Treatment of the iodide IV with cyclopentadiene and triethylamine in refluxing tetrahydrofuran produced cyclobutadiene(π-cyclopentadienyl)cobalt together with π-cyclopentadienylcobalt dicarbonyl which were separated by chromatography.

Cyclobutadiene(π-cyclopentadienyl)cobalt forms yellow crystals from pentane, mp 83–85°. The nmr spectrum of the compound consists of two sharp singlets at τ 5.14 and 6.39 having areas of 5:4, respectively. The mass spectral cracking pattern shows, among others, prominent peaks at 176 (56%), 150 (28%), and 124 (100%) corresponding to the parent molecular ion and the ions following loss of C_2H_2 and C_4H_4 fragments, respectively. When kept under nitrogen the compound is stable, but in air it appears to undergo very slow oxidative decomposition.

In view of the extensive substitution reactions known to occur on the ligand rings in ferrocene, the question as to whether similar aromatic character would be exhibited by the complex I is of interest. Furthermore, since the cyclobutadiene ligand in the complex cyclobutadieneiron tricarbonyl readily participates in electrophilic substitution reactions[6] and, as Rausch and Genetti have recently shown, the cyclopentadienyl ring in tetraphenylcyclobutadiene(π-cyclopentadienyl)cobalt can also be substituted,[7] then the question as to the relative reactivity of the two rings in I is an additional point of interest.

Initial results indicate that electrophilic substitution reactions do occur with the complex I and that the cyclobutadiene ring is much more reactive in this respect than the cyclopentadienyl ring. Treatment of I with acetyl chloride and aluminum chloride affords the acetyl derivative V; however, under the conditions used[8] extensive decomposition occurred and the yield of V was poor (*ca.* 10%). The acetyl derivative showed nmr absorptions at τ 5.13, 5.72, 6.15, and 8.12 having areas of 5:2:1:3, respectively. Acetoxymercuration with Hg(OAc)$_2$ in acetic acid produces the acetoxy-

[1] A. Nakamura and H. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

[2] R. Bruce and P. M. Maitlis, *Can. J. Chem.*, **45**, 2017 (1967).

[3] R. G. Amiet, P. C. Reeves, and R. Pettit, *Chem. Commun.*, in press.

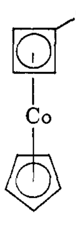
[4] An early product in reaction is cyclobutadienecobalt dicarbonyl chloride which appears to react rapidly with NaCo(CO)$_4$ to produce III; hence, 2 moles of NaCo(CO)$_4$ is used.

[5] The elemental analysis of this material and the other new compounds reported in this paper were in satisfactory agreement with expected values.

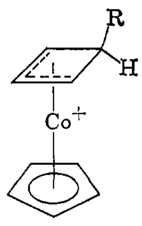
[6] J. D. Fitzpatrick, L. Watts, G. F. Emerson, and R. Pettit, *J. Am. Chem. Soc.*, **87**, 3254 (1965).

[7] M. D. Rausch and R. A. Genetti, *ibid.*, **89**, 5502 (1967).

[8] Under the same conditions cyclobutadieneiron tricarbonyl affords the acetyl derivative in 95% yield.



V



VI

mercury derivative of I in high yield, and again it appears that only the cyclobutadiene ring is attacked. Mercuration conducted in CH_3COOD followed by decomposition in D_2O afforded a mixture of mono-, di-, tri-, and tetradeuterio derivatives of complex I. Mass spectral analysis of this mixture clearly indicated that the great majority of the substitutions occurred on the cyclobutadiene ring, and little, if any, took place on the cyclopentadienyl ring. The reactivity of the C_4 ligand in this system could reasonably be associated with the well-established stability of π-allylcobalt complexes. An allylcobalt system such as VI could be expected to be a relatively stable intermediate in the substitution process and result in the greater reactivity of the cyclobutadiene ligand.

[9] The authors thank the National Science Foundation, the U. S. Army Research Office (Durham), and the Robert A. Welch Foundation for financial support. We also thank Badische Anilin und Soda Fabrik for a generous gift of cyclooctatetraene.

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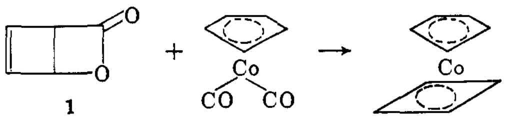
Photochemical Synthesis of Cyclobutadiene(cyclopentadienyl)cobalt

Sir:

Recently we reported the preparation of cyclobutadieneiron tricarbonyl[1] from iron pentacarbonyl or iron enneacarbonyl and photo-α-pyrone (**1**).[2] We now find that photolysis[3] of an ethereal solution of **1** and cyclopentadienylcobalt dicarbonyl (**2**) leads to the formation of cyclobutadiene(cyclopentadienyl)cobalt (**3**), a substance, isoelectronic with ferrocene, possessing an unsubstituted cyclobutadiene ring.[4]



1 **2** **3**

Cyclobutadiene(cyclopentadienyl)cobalt (**3**) is a yellow, crystalline material, mp 88.5–89.0°, which sublimes readily at atmospheric pressure, is soluble in the common organic solvents, and exhibits a high degree of stability in air. *Anal.* Calcd for C_9H_9Co: C, 61.36; H, 5.11. Found: C, 61.25; H, 5.20.

The mass spectrum (70 ev) of **3** is relatively simple, with three intense peaks at m/e 176 (molecular ion), 150, and 124, lower intensity peaks at m/e 98, 85, and 59, and metastables at m/e 127.8, 102.5, and 77.5 for the transitions $176 \rightarrow 150$, $150 \rightarrow 124$, and $124 \rightarrow 98$. The molecular ion accounts for almost 40% of the total ion current, reflecting the high stability of the complex.

The presence of a cyclobutadiene ring in the complex is supported by its nmr spectrum (CCl_4), which exhibits two singlet peaks at τ 5.10 and 6.34 (relative areas 5:4) assigned to cyclopentadienyl and cyclobutadiene ring protons, respectively. The former are therefore significantly deshielded compared with those in ferrocene (τ 5.96, CCl_4),[5] while the latter are somewhat more shielded than the ring protons in cyclobutadieneiron tricarbonyl (τ 6.00, CCl_4).[2]

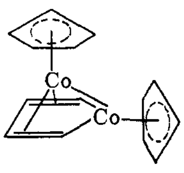
The most striking evidence for structure **3** is provided by its infrared spectrum (KBr) which exhibits peaks at 3090, 3060, 1408, 1308, 1210, 1101, 997, 926, 815, 787 (sh), 775, 749 (sh), and 739 (sh) cm^{-1}, in addition to a series of weak bonds between 1450 and 1800 cm^{-1}. Its spectrum is therefore very nearly a composite of the spectra of ferrocene (KBr, 3084, 1407, 1101, 999, 813, 787 cm^{-1}) and, excluding the carbonyl carbonyl bands, of cyclobutadieneiron tricarbonyl (CS_2, 3100, 1320, 1230, 934, 817, 770 cm^{-1}).

The uv spectrum of the complex (95% EtOH) exhibits three absorption maxima at 258, 290, and 385 mμ (ε 20,000, 1200, and 320).

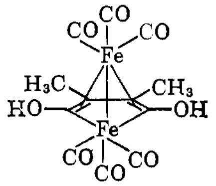
In addition to **3**, a dark green, air-sensitive crystalline material, mp 121–122°, is formed in the photolysis of **2** and **1**. *Anal.* Calcd for $C_{14}H_{14}Co_2$: C, 56.00; H, 4.67. Found: C, 56.21; H, 4.73.

Its mass spectrum (70 ev) exhibits principal peaks at m/e 300 (molecular ion), 241, 239, 222, 189, 143, 124, and 118. Its infrared spectrum shows all the peaks characteristic of the cyclopentadienyl ring, but there is no comparable correlation of spectral bands indicative of a cyclobutadiene ring chromophore. The nmr spectrum (CCl_4) of this substance exhibits an apparent triplet at unusually low field (τ 1.79, J = 3.5 Hz) and two singlet peaks at τ 5.04 (fine structure partially hidden underneath) and 5.16, with relative integrated areas of 2:7:5.

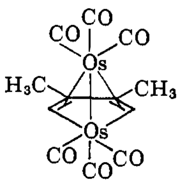
On the basis of these data, structure **4** is tentatively suggested for this substance. Such a structure is closely related to those of the iron complex **5**,[6] formed in the reaction of dimethylacetylene with an alkaline solution of iron carbonyl hydride, and the osmium complex **6**,[7] prepared by the reaction of $Os_3(CO)_{12}$ with 2,3-dimethylbutadiene. The chemistry of these new cobalt complexes is under investigation.



4



5



6

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

[2] M. Rosenblum and C. Gatsonis, *ibid.*, **89**, 5074 (1967).

[3] Irradiation was carried out with a mercury arc lamp (Hanovia, Type L, 450 W) with a Corex glass filter. The products were isolated and purified by column chromatography on alumina. All operations were conducted in a nitrogen atmosphere.

[4] The tetraphenyl derivative of **3**, prepared from cyclopentadienylcobalt dicarbonyl and diphenylacetylene, has been reported by A. Nakamura and H. Hagihara, *Bull. Chem. Soc. Japan*, **34**, 452 (1961).

[5] M. Rosenblum, "Chemistry of the Iron Group Metallocenes," Interscience Publishers, Inc., New York, N. Y., 1965.

[6] A. A. Hock and O. S. Mills, *Acta Cryst.*, **14**, 139 (1961).

[7] R. P. Dodge, O. S. Mills, and V. Schomaker, *Proc. Chem. Soc.*, 380 (1963).