

synthesis of the phenanthrenequinone trianion radical and comparison of its spectral properties with those of the trianion radical obtained from benzil. Thus, both routes produce a trianion radical which gives a five-line e.p.r. spectrum (coupling with the four starred protons) and absorbs in the visible region at 555 and 410 m μ .

The HMO calculations indicate that, whereas the NBMO being filled at the Bz_2^- and $Bz_2^{=}$ stages is predominantly an α -diketone MO, that which accommodates the third electron is largely of the *cis*-stilbene type, with high spin density on the phenyl rings at the *ortho* and *para* positions. The similar fate of $Bz_2^{=}$ and photoexcited *cis*-stilbenes⁴ suggests a possible parallel between reactions of highly electronated and photoexcited molecules.

Calculations for the oxalate system also show an MO at $\alpha - 0.73\beta$ which is vacant at the dianion stage. Again, excess potassium is found to convert the dianion, sodium oxalate, into a stable, purple trianion radical showing an e.p.r. singlet.



A detailed report of the e.p.r. spectra of these and other trianion radicals will be forthcoming at a later date.

(4) R. Srinivasan and J. C. Powers, *J. Am. Chem. Soc.*, **85**, 1355 (1963); F. B. Mallony, *et al.*, *ibid.*, **84**, 4361 (1962).

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RECEIVED MAY 12, 1964

A Krypton Difluoride-Antimony Pentafluoride Complex¹

Sir:

Krypton difluoride has recently been prepared in these laboratories by an electric discharge method.² This compound, though manifestly less stable than xenon difluoride,³ might be expected to show an analogous chemistry. Recently it has been shown that xenon difluoride interacts with antimony pentafluoride to form a stable complex of composition $XeF_2 \cdot 2SbF_5$,⁴ and now we report the preparation of the analogous complex $KrF_2 \cdot 2SbF_5$. The compound is formed by treating krypton difluoride with antimony pentafluoride in glass or Kel-F. Reaction is complete at -20° , and if excess antimony pentafluoride is present, most of the white crystalline material formed dissolves to give a clear yellowish solution at room temperature. The white complex can be recovered from the solution by pumping away the solvent at 25° . Two separate specimens gave the following analytical results: (1) sample weight 0.875 g.; Kr, 15.7%; Sb, 42.4%; and F, 41.9%; (2) sample weight 0.189 g.; Kr, 14.2%, Sb, 44.2%; and F, 41.6%. $KrF_2 \cdot 2SbF_5$ requires Kr, 15.1%; Sb, 43.8%; F, 41.0%.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) F. Schreiner, J. G. Malm, and J. C. Hindman, to be published.

(3) D. R. MacKenzie, *Science*, **141**, 1171 (1964).

(4) A. J. Edwards, J. H. Holloway, and R. D. Peacock, *Proc. Chem. Soc.*, 275 (1965).

The complex $KrF_2 \cdot 2SbF_5$ is more stable and much less volatile than the parent difluoride. For example, a sample weighing 0.848 g. lost only 0.020 g. on pumping for 20 hr. at 25° . It melts at about 50° , but the liquid decomposes quickly to antimony pentafluoride, krypton, and fluorine. The complex also decomposes slowly in antimony pentafluoride solution at 25° . As expected, it is an extremely reactive material and ignites organic matter explosively. Solutions of $KrF_2 \cdot 2SbF_5$ in antimony pentafluoride appear to attack Kel-F. Aqueous hydrolysis in basic or slightly acidic solution yields not only the expected krypton and oxygen, but also appreciable quantities of fluorine monoxide. The infrared spectrum of the complex shows a strong characteristic absorption band at 813 cm^{-1} and other strong, poorly resolved absorptions in the 600–700 cm^{-1} region.

Preliminary experiments show that krypton difluoride combines with arsenic pentafluoride at -78° , but the adduct is very unstable and we have been unable to isolate it.

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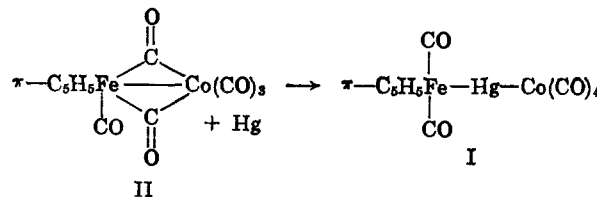
RECEIVED AUGUST 10, 1964

An Organometal Carbonyl Containing Covalent Bonds from Iron to Mercury to Cobalt

Sir:

Mercury salts of binuclear metal carbonyls, such as $Hg[Co(CO)_4]_2$,¹ $Hg[Mn(CO)_5]_2$,² and those of cyclopentadienyl derivatives of metal carbonyls, such as $Hg[\pi-C_5H_5M(CO)_n]_2$,^{3,4} where $n = 2$ or 3 and $M = Mo, Cr, \text{ or } Fe$, are known. Although all of these compounds possess three metals covalently bonded, they are all symmetrical, consisting of two identical metal carbonyl portions bonded through mercury. For this reason they are usually referred to as mercury salts. In an extension of our mercury insertion reaction,⁵ we have synthesized what is to the best of our knowledge the first example of a compound containing three different metals covalently bonded.

The new compound, π -cyclopentadienyldicarbonyl-iron mercury cobalt tetracarbonyl, $\pi-C_5H_5Fe(CO)_2 \cdot HgCo(CO)_4$ (I), was prepared by simply stirring a solution of π -cyclopentadienylmonocarbonyliron μ -dicarbonyl cobalt tricarbonyl⁶ (II) in hexane with mercury under an atmosphere of carbon monoxide at room temperature for 48 hr.



On stirring, the dark red (almost black) solution very gradually changed to dark orange. The orange

(1) W. Hieber and H. Schulten, *Z. anorg. allgem. Chem.*, **232**, 17 (1937).

(2) W. Hieber and W. Schropp, Jr., *Chem. Ber.*, **93**, 455 (1960).

(3) E. O. Fischer, W. Hafner, and H. O. Stahl, *Z. anorg. allgem. Chem.*, **282**, 47 (1955).

(4) E. O. Fischer and R. Böttcher, *Z. Naturforsch.*, **10b**, 600 (1955).

(5) S. V. Digne and M. Orchin, *Inorg. Chem.*, **1**, 965 (1962).

(6) K. K. Joshi and P. L. Pauson, *Z. Naturforsch.*, **17b**, 565 (1962).

solution was filtered; the filtrate was concentrated to half its original volume and stored overnight at 0° under carbon monoxide. The orange crystals were filtered and the filtrate was cooled in a bath of Dry Ice-acetone, whereupon a yellow precipitate was obtained. The crystals and the second crop of precipitate were recrystallized separately from *n*-pentane and proved to be identical. After four such recrystallizations, orange crystals melting at 93–94° with slight decomposition were obtained.

Anal. Calcd. for $C_{11}H_5CoFeHgO_6$: C, 24.13; H, 0.91; mol. wt., 547. Found⁷: C, 24.14; H, 1.14; mol. wt.,⁸ 523.

The X-ray emission spectrum showed bands corresponding to Hg $L\alpha_1$ at 35.90, Co $K\alpha_1$ at 52.75, and Fe $K\alpha_1$ at 57.47°.

It is soluble in most organic solvents but insoluble in water. It is air stable as a solid but decomposes slowly in solution on exposure to air. On treatment with an aqueous iodine solution (KI + I₂ in water) 4 moles of CO are evolved per mole of the compound, and π -C₅H₅Fe(CO)₂I,⁹ m.p. 118–120° dec., is recovered. I reacts with excess triphenylphosphine in hexane solution with the evolution of 1 mole of CO per mole of I to yield a bright yellow, insoluble, air-stable compound. This compound was difficult to purify because of its limited solubility.

The infrared spectra in the C–O stretching region of I and II in carbon tetrachloride solution showed the following bands: I (cm.⁻¹): 1952 (m), 1972 (sh), 1983 (s), 1990 (s), 2008 (s), 2054 (sh, w), and 2066.6 (s); II (cm.⁻¹): 1830 (m), 1961 (sh), 1985 (s), 2021 (s), 2063 (m), 2075 (s), and 2130 (w).

I probably has the geometry of two trigonal bipyramids connected at corners through mercury. It may be considered as being derived from half of Hg[π -C₅H₅Fe(CO)₂]₂ and half of Hg[Co(CO)₄]₂, both of which are also probably trigonal bipyramids. However, the spectrum of I shows some interesting differences from the two moieties above and this will be the subject of a future paper.

Acknowledgment.—We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of the above research. We also thank Frank Rizzo for help with the X-ray emission spectra.

(7) Microanalyses were performed by Galbraith Laboratories, Knoxville, Tenn.

(8) Determined in benzene using a Mechrolab vapor pressure osmometer.

(9) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **2**, 38 (1956).

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RECEIVED JULY 30, 1964

Crystallographic Studies of Krypton Difluoride¹

Sir:

The identification of KrF₂ has been established by Turner and Pimentel² and MacKenzie.³ Samples of the difluoride, prepared by J. Malm and F. Schreiner in this laboratory, have been found to be sufficiently

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) J. J. Turner and G. C. Pimentel, *Science*, **140**, 974 (1963).

(3) D. R. MacKenzie, *ibid.*, **141**, 3586 (1963).

stable to enable us to obtain some crystallographic information.

Single crystal oscillation and Weissenberg patterns indicate that the symmetry is tetragonal, with $a = 6.533$ and $c = 5.831$ Å. The calculated X-ray density, assuming four molecules in the cell, is 3.24 g./cm.³.

It is not possible to establish the space group on the basis of the available X-ray data. However, the cell appears to be primitive, and KrF₂ is therefore not isostructural with XeF₂. The latter is also tetragonal, with $a = 4.315$ and $c = 6.990$ Å., but is based on a body-centered cell with space group I4/mmm.

The quality of the X-ray patterns is poor because of a tendency for the crystals to decompose upon irradiation. Hence, the assignment of the symmetry is tentative until further structural studies are completed.

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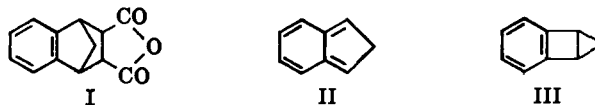
STANLEY SIGEL
ELIZABETH GEBERT

RECEIVED JULY 20, 1964

Formation and Capture of a Reactive Intermediate Related to Dimethylpseudoindene¹

Sir:

The formation of benzenorbornene derivatives (*e.g.*, I) from the reaction of maleic anhydride with indene^{2–4} (or from the zinc debromination of 1,3-dibromoindane in the presence of maleic anhydride³) and the thermal 1,5-hydrogen rearrangements of indene⁵ are readily interpreted on the assumption that isoindene (II)



intervenes as an intermediate. The possibility that a valency tautomer, pseudoindene (III, benzobicyclo[2.1.0]pentene), may be capable of existence prompted the present study.

Pseudoindene (III) is a formal cycloaddition product of benzyne and cyclopropene. In attempting to realize this type of addition in practice, we observed that 1,2,3-triphenylcyclopropene⁶ (IV) and benzyne⁷ (V) did not react in this sense but instead gave the substitutive addition product 1,2,3,3-tetraphenylcyclopropene (VI), m.p. 177–178°, in 60–70% yield.¹⁰ The structure of VI was assigned on the basis of its elemental composition. *Anal.* Calcd. for C₂₇H₂₀: C, 94.15; H, 5.85; mol. wt., 344. Found: C, 93.85; H, 5.97; mol. wt. 383, 325 (osmometric). Spectral peaks appeared at: ultraviolet λ_{\max} (ethanol) 229, 303, 316,

(1) The support of this work by the Directorate of Chemical Sciences, Air Force Office of Scientific Research, through Grant No. AF-AFOSR-389-63, and by the National Science Foundation through a fellowship, is gratefully acknowledged.

(2) K. Alder, F. Pascher, and H. Vagt, *Ber.*, **75**, 1501 (1942).

(3) K. Alder and M. Fremery, *Tetrahedron*, **14**, 190 (1961).

(4) J. A. Berson and G. B. Aspelin, *ibid.*, in press.

(5) W. R. Roth, *Tetrahedron Letters*, No. 17, 1009 (1964).

(6) R. Breslow and P. Dowd, *J. Am. Chem. Soc.*, **85**, 2729 (1963).

(7) Generated *in situ* from an ethylene chloride suspension of *o*-benzenediazonium carboxylate according to a modification⁸ of the Stiles⁹ procedure. We are indebted to Prof. L. Friedman for details.

(8) L. Friedman, private communication.

(9) M. Stiles, R. G. Miller, and U. Burckhardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

(10) This kind of process seems to be analogous to the thermal dimerization of IV to VII.⁶