The derived distances[8] in $(HF_2)^-$, uncorrected for thermal motion, are F(1)–F(2), 2.260 (4); F(2)–H, 1.025 (6); and F(2)–H, 1.235 (6) Å. This compound crystallizes in the orthorhombic space group *Pbca*, with $Z = 8$ and cell dimensions $a = 7.171$ (4), $b = 18.423$ (11), and $c = 11.839$ (7) Å at 22 ± 2°. The observed and calculated densities are 1.27 and 1.25 g/cm^3, respectively.

Two complete octants (twice the amount required) of three-dimensional data were collected, yielding 2715 reflections [2007 with $(F_o) > 1\sigma(F_o)$], at 22 ± 2° to sin $\theta/\lambda = 0.62$ at the Argonne National Laboratory CP-5 neutron source ($\lambda = 1.142$ (1) Å). All data were corrected for absorption ($\mu = 2.36$ cm^{-1}) and scaled against a standard NaCl crystal. The initial positional parameters for C, N, and F were those given in an X-ray study.[9] All hydrogen atoms were precisely located using Fourier maps. Full-matrix least-squares calculations (with anisotropic thermal parameters and an isotropic extinction correction) have led, at this stage, to a value of the reliability index of $R(F_o) = 0.078$ using all data with $(F_o) > 1\sigma(F_o)$. The present ratio of observations to parameters is 2008:191. A difference Fourier map, calculated to remove all atoms except the hydrogen atom of $(HF_2)^-$, yielded positional coordinates in complete agreement with the least-squares results. A total difference Fourier synthesis was virtually featureless, thus confirming the least-squares results.

The structure is comprised of discrete $CH_3C_6H_4NH_3^+$ cations and $(F–H--F)^-$ anions. This is the first known example in which the $(HF_2)^-$ ion, illustrated in Figure 1, possesses an asymmetric hydrogen bond. The F–H distances ($\sigma = 0.006$ Å) and (F–H--F) bond angle of 178.1 (5)° indicate that the anion is essentially linear. The short F–H distance of 1.025 (6) Å is ~0.108 Å longer than in gaseous HF. Finally, the F–F separation of 2.260 (4) Å is identical (±0.01 Å) with that reported for the bifluoride salts of Na^+ (2.264 (3) Å),[3] K^+ (2.277 (6) Å),[3] and NH_4^+ (2.269 (5), 2.275 (5) Å).[10] The C–C and C–N distances derived in this study agree within the standard deviations reported in the X-ray study ($\sigma = 0.009$ Å).[9]

We feel that the unusual hydrogen bond configuration observed for the anion is a consequence of its very asymmetric near-neighbor (hydrogen bonding) environment. As shown in Table I, atoms F(1) and F(2) each have two near-neighbor H atoms (from $-NH_3^+$ groups of the cation) but with very different F···H(N) distances. Clearly, F(1) is much more rigidly bound than F(2) by strong hydrogen bond formation as is evidenced by its short F···H(N) distances and diminished thermal motion, as illustrated in Figure 1.

Table I. Bifluoride Ion Near-Neighbor Distances

Atom	Neighbors	F···H distances, Å
F(1)	H(N)	1.608, 1.675
F(2)	H(N)	1.777, 2.518

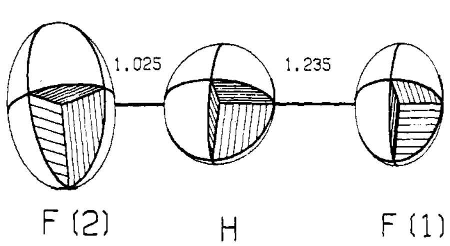


Figure 1. Bond distances in the asymmetric bifluoride ion. The thermal ellipsoids are scaled to enclose 50% probability.

This rather remarkable finding suggests to us that the well-known "symmetric" hydrogen bond only arises whenever the combined electronic and crystal environment about an ion lacks sufficient asymmetry to distort the potential surface "seen" by the bridging hydrogen atom. These results, and those derived from the study[11] of very short (O–H–O) bonds, suggest that regardless of the "shortness" of the X--X bond in the $(X–H–X)^{\pm}$ moiety the molecular geometry of the hydrogen bond is strongly dependent on the near-neighbor environment.

Additional investigations including infrared, Raman, and nmr spectroscopic studies are in progress. Deuterated material is being prepared prior to a neutron diffraction study of the isotope effect on the $(F–D–F)^-$ bond. The full structural study will be reported at a later date.

---

(8) Numbers given in parentheses are estimated standard deviations in the least significant digit of the given parameters.

(9) W. A. Denne and M. F. Mackay, *J. Cryst. Mol. Struct.*, **1**, 311 (1971).

(10) T. R. R. McDonald, *Acta Crystallogr.*, **13**, 113 (1960).

(11) J. M. Williams, S. W. Peterson, and H. A. Levy, American Crystallographic Association, Program Abstracts 17, Albuquerque, N. M., 1972.

(12) CSUI research student with ACEA from the College of Notre Dame, Baltimore, Md.

Jack M. Williams,* Lynn F. Schneemeyer[12]
Chemistry Division, Argonne National Laboratory
Argonne, Illinois 60439

Received May 15, 1973

New Heterocyclic Five-Membered Metallo-Ring Complexes of Cobalt and Rhodium

Sir:

Previously, one of the authors showed the formation of five-membered "cobaltacyclopentadiene" complexes by the reaction of substituted acetylenes and cobalt-tolan complex, π-$C_5H_5Co(PPh_3)(PhC{\equiv}CPh)$ (**2a**), which is formally regarded as a three-membered ring compound containing cobalt.[1] Five-membered heterocyclic ring complexes have also been prepared by the reactions of three-membered ring complexes, *i.e.*, dioxygen–, hexafluoroacetone–, and hexafluoroisopropylideneamine–metal complexes with aldehydes, ketones, and hexafluoroisopropylidenamine.[2,3] Recently, an insertion reaction of hexafluoro-but-2-yne and CO molecules into the five-membered cyclic cobalt–azobenzene complex has been reported.[4] These studies suggest that there may be many potential metallo-ring

---

(1) H. Yamazaki and N. Hagihara, *J. Organometal. Chem.*, **21**, 431 (1970).

(2) (a) R. Ugo, F. Conti, S. Cenini, R. Mason, and G. B. Robertson, *Chem. Commun.*, 1498 (1968); (b) P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *J. Amer. Chem. Soc.*, **92**, 5873 (1970); (c) P. J. Hayward and C. J. Nyman, *ibid.*, **93**, 617 (1971).

(3) H. D. Empsall, M. Green, and F. G. A. Stone, *J. Chem. Soc. A*, 96 (1972), and references therein.

(4) M. I. Bruce, B. L. Goodall, A. D. Redhouse, and F. G. A. Stone, *J. Chem. Soc., Chem. Commun.*, 1228 (1972).

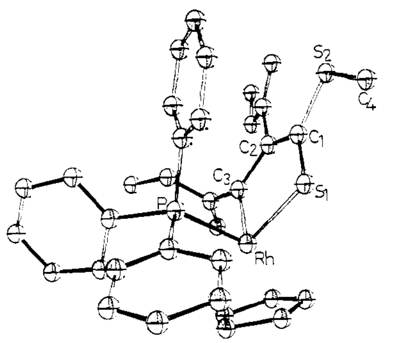
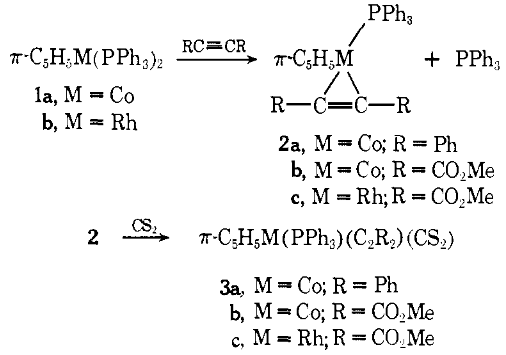


Figure 1. The geometry of the $[\pi\text{-}C_5H_5Rh(PPh_3)[C_2(CO_2Me)_2](CS_2Me)]^+$ ion. The I^- ion and crystallization solvent have been omitted for clarity.

transformations, which, if properly used, could provide organic heterocyclic compounds.

We wish to report here new heterocyclic five-membered metallo-ring complexes of cobalt and rhodium, which have been prepared by the stepwise reaction of bis(triphenylphosphine)-π-cyclopentadienylmetal (**1a** or **1b**)[5] with acetylenes and carbon disulfide.



$\pi\text{-}C_5H_5M(PPh_3)_2 \xrightarrow{RC\equiv CR} \pi\text{-}C_5H_5M(PPh_3)(RC\equiv CR) + PPh_3$

1a, M = Co
b, M = Rh

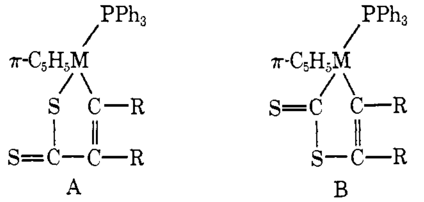
2a, M = Co; R = Ph
b, M = Co; R = CO_2Me
c, M = Rh; R = CO_2Me

$2 \xrightarrow{CS_2} \pi\text{-}C_5H_5M(PPh_3)(C_2R_2)(CS_2)$

3a, M = Co; R = Ph
b, M = Co; R = CO_2Me
c, M = Rh; R = CO_2Me

The reaction of the cobalt-tolan complex (**2a**) with excess carbon disulfide in benzene at room temperature gives a 48% yield of purple-brown crystalline $\pi\text{-}C_5H_5Co(PPh_3)(C_2Ph_2)(CS_2)$ (**3a**), 174–176° dec, isolated by chromatography and purified by crystallization from benzene–hexane. Similarly, red-brown crystals of $\pi\text{-}C_5H_5Co(PPh_3)[C_2(CO_2Me)_2](CS_2)$ (**3b**), 193–197° dec, are obtained in 77% yield from **2b** and CS_2. The rhodium analog (**2c**)[6] reacts at a higher temperature (70°) to give orange-red crystals of $\pi\text{-}C_5H_5Rh(PPh_3)[C_2(CO_2Me)_2](CS_2)$ (**3c**), 202–205° dec, in 90% yield.

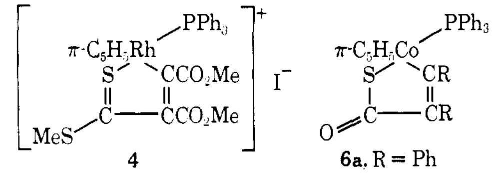
Complexes **3b** and **3c** showed virtually identical ir spectra. The ^1H nmr spectra showed the presence of two different types of carbomethoxy protons at τ 6.37 and 6.41 for **3b**, and τ 6.38 and 6.44 for **3c**. Two possible isomeric structures for **3** are A and B. Like usual organic sulfur compounds, complex **3c** reacts with methyl iodide to form orange crystalline methiodide (**4**), 145–148° dec, and a single-crystal X-ray analysis of complex **4** has been carried out to determine the structure of **3**.[7] Crystal data are: $a = 10.194$ (2), $b =$



16.09 (4), $c = 9.924$ (2) Å; $\alpha = 84.97$ (9), $\beta = 93.31$ (2), $\gamma = 91.62$ (3)°; $V = 1619$ Å^3; $d_{measd} = 1.70$, $d_{calcd} = 1.72$ g/cm^3 (assuming 0.5 mol of CH_2Cl_2 per mol of complex) for $Z = 2$; space group $P\bar{1}$. The structure determination was based on 2280 independent reflections, collected on a Rigaku automatic diffractometer using crystal monochromated Mo Kα radiation. The block diagonal least-squares refinement converged to a conventional R value of 11%. The molecule consists of a cyclopentadienyl group, triphenylphosphine, and $\overline{Rh\text{-}S\cdot C\cdot C\cdot C}$ metallo-ring, thus establishing structure A for complexes **3** (Figure 1). The methyl group originated from MeI is bonded to the thiocarbonyl sulfur (S_2). The five-membered metallo-ring has a good planarity, with a Rh–S_1 distance of 2.29 Å and a Rh–C_3 distance of 1.99 Å.

The carbon disulfide complex of rhodium, $\pi\text{-}C_5H_5Rh(PPh_3)(CS_2)$,[8] reacts with dimethyl acetylenedicarboxylate in benzene at 70° to give orange crystals (**5**), 172–178° dec. The composition of complex **5** is identical with that of complex **3c**, but their spectra are different; the ^1H nmr spectrum shows two different carbomethoxy groups at τ 6.39 and 6.74. Structure B may be assigned to this complex.[9]

Carbonyl sulfide, as well as CS_2, reacts with **2a** or **2b**. Thus on treatment of SCO with a benzene solution of **2a** or **2b** at room temperature, brown crystals of $\pi\text{-}C_5H_5Co(PPh_3)(C_2Ph_2)(SCO)$ (**6a**) and $\pi\text{-}C_5H_5Co(PPh_3)[C_2(CO_2Me)_2](SCO)$ (**6b**) are formed in 9 and 43% yields, respectively. The ir spectra exhibit strong bands at 1610 cm^{-1} for **6a** and 1622 cm^{-1} for **6b**, which are attributable to the stretching mode of carbonyl groups derived from SCO. Since **6a** is also obtained by the oxidation reaction of **3a** with PhNO at 70°



4

6a, R = Ph
b, R = CO_2Me

---

[5] The preparation of **1a** or **1b** is described in H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jap.*, 44, 2260 (1971). But they can be prepared more conveniently according to the equation

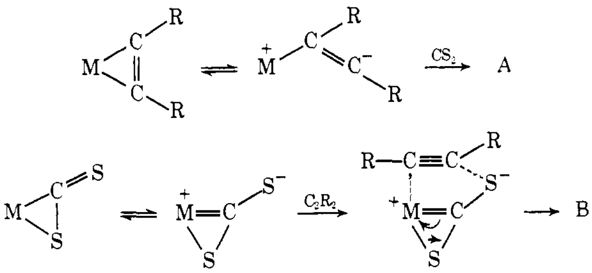
$$(PPh_3)_3MCl + C_5H_5Na \longrightarrow \pi\text{-}C_5H_5M(PPh_3)_2 + PPh_3 + NaCl \quad (M = Co \text{ or } Rh)$$

[6] Complex **2c** is obtained in better yield by the reaction of $(PPh_3)_3RhCl$ with dimethyl acetylenedicarboxylate and thallium cyclopentadienide.

[7] Although complex **3c** is crystalline, the crystals obtained were too small for X-ray analysis.

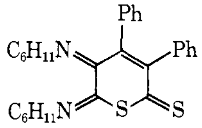
[8] This complex was prepared by the reaction of **1b** with CS_2. Y. Wakatsuki and H. Yamazaki, *J. Organometal. Chem.*, in press.

[9] Clearly, a variety of different reaction paths may be proposed to explain the formation of complexes of structures A and B. One of the probable mechanisms is shown below, in which the metal–acetylene or metal–CS_2 complex behaves as a 1,3-dipolarophile.



(13% yield), the structure illustrated was assigned to complex **6**.

In attempts to release the heterocyclic rings from these metallo-rings, we found that complex **3a** reacts with sulfur in benzene at 70° to afford 4,5-diphenyl 1,2-dithia-4-cyclopentene-3-thione, mp 160° (lit.[10] 159.5°), in almost quantitative yield. Cyclohexyl isocyanide also reacts with **3a** in a similar condition to give a 21% yield of pale yellow crystals (**7**) of the formula $C_{29}H_{32}N_2S_2$, mp 203°, mol wt 472 (mass spectrum), 472.7 (calcd). The structure of this compound may be written as shown below.



7

More extensive study on this type of reaction is in progress.

---

[10] A. Lüttinghaus, H. B. König, and B. Böttcher, *Justus Liebigs Ann. Chem.*, **560**, 201 (1948).

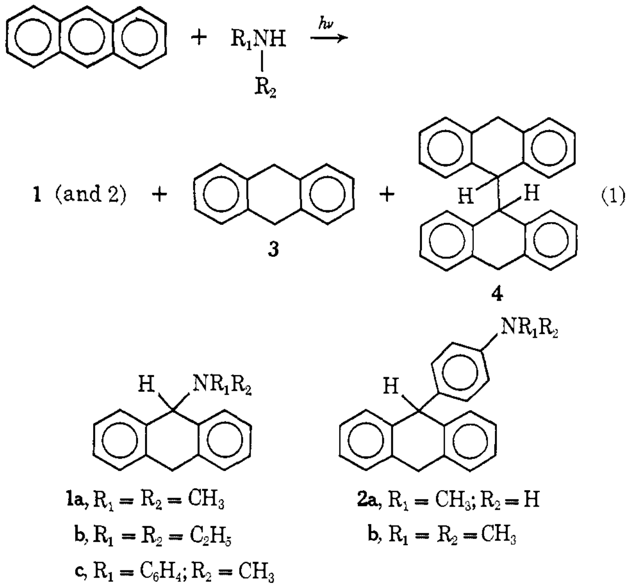
Yasuo Wakatsuki,* Hiroshi Yamazaki, Hitoshi Iwasaki
The Institute of Physical and Chemical Research
Wako-shi, Saitama 351, Japan

Received April 27, 1973

Chemistry of Exciplexes, Photochemical Addition of Secondary Amines to Anthracene

Sir:

Weller and his associates demonstrated that photoexcited arenes form exciplexes with tertiary amines which exhibit exciplex emission in nonpolar solvents.[1] Their contributions stimulated extensive investigations in this area.[2-7] In connection with their studies on arene–tertiary amine exciplexes, Mataga[2] and Nakajima[3] reported that secondary amines also quench the fluorescence of arenes but no exciplex emission was observed. This marked difference between the behaviors of these two groups of amines was, however, not understood. In this communication we wish to report that anthracene undergoes facile photochemical reactions with secondary amines in benzene and in acetonitrile. Mechanistic investigations suggested that these reactions proceed *via* exciplexes as intermediates and an important step in the decay of these exciplexes may involve the proton transfer from the secondary amine to the arene.



Irradiation of a solution of anthracene (0.01–0.05 *M*) and dimethylamine, diethylamine, or *N*-methylaniline (1.0 *M*) in benzene or in acetonitrile yielded both the 1:1 adduct(s) and the reduction products of anthracene (reaction 1). The 1:1 adduct was the 9-amino-9,10-dihydroanthracene (**1a–c**), respectively, but **1c** was accompanied with minor amounts of 9-(*p*-methylaminophenyl)-9,10-dihydroanthracene (**2a**). The reaction may thus be applied for the amination of anthracene at the meso position. Irradiation of anthracene with diethylamine-*d* resulted in the formation of photoproducts **1b**, **3**, and **4** containing deuterium at the meso positions. This observation suggests that proton transfer from the amine to anthracene may be involved in the formation of these products. On the other hand, irradiation of anthracene and *N*,*N*-dimethylaniline in benzene yielded exclusively the photodimer of anthracene but in acetonitrile it yielded a mixture of **2b**, **3**, and **4**.[8] We found that different amines quench the fluorescence of anthracene with different quenching efficiencies and that the quenching efficiencies are solvent dependent (Table I), amines with lower ionization potentials are more efficient quenchers and the quenching efficiencies are higher in acetonitrile than in benzene. We also observed that quantum yields of the consumption of anthracene in the presence of amines

Table I. Quenching of Anthracene Fluorescence by Amines[a]

Amine	IP, eV	Solvent	$k_q\tau$, mol^{-1} l.	C_h, *M*[b]
$C_6H_5N(C_2H_5)_2$	7.15[c]	CH_3CN	91.0, 88.2[d]	0.011 ± 0.0005
		C_6H_6	39.0	0.026 ± 0.0005
$C_6H_5NHCH_3$	7.34[c]	CH_3CN	78.5	0.0125 ± 0.0005
		C_6H_6	22.3	0.0448 ± 0.0005
$(C_2H_5)_2NH$	8.44[c]	CH_3CN	14.0	0.072 ± 0.002
		C_6H_6	3.1	0.324 ± 0.010
$(C_2H_5)_2ND$[e]		CH_3CN	12.2	0.082 ± 0.002
		C_6H_6	2.8	0.358 ± 0.010

[a] Anthracene concentration, 5×10^{-4} *M*; excitation at 350 nm. [b] Half-quenching concentrations. [c] V. I. Vedeneyev, L. V. Gurvich, V. N. Kondrat'yev, V. A. Medvedev, and Ye. L. Frankevich, "Bond Energies, Ionization Potentials and Electron Affinities," E. Arnold, London, 1966. [d] A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968). [e] Isotopic purity, 80%.

---

[1] A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968), and references therein.

[2] N. Nakashima, N. Mataga, F. Ushio, and C. Yamanaka, *Z. Phys. Chem. (Frankfurt am Main)*, **79**, 150 (1972); N. Mataga, *et al.*, *Bull. Chem. Soc. Jap.*, **40**, 1355 (1967).

[3] A. Nakajima, *ibid.*, **42**, 3409 (1969).

[4] R. J. McDonald and B. K. Selinger, *Aust. J. Chem.*, **24**, 1797 (1971).

[5] H. Knibbe, D. Rehm, and A. Weller, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 95 (1967).

[6] Y. Taniguchi and N. Mataga, *Chem. Phys. Lett.*, **13**, 596 (1972).

[7] C. R. Goldschmidt, R. Potashnik, and M. Ottolenghi, *J. Phys. Chem.*, **75**, 1025 (1971); N. Orbach, R. Potashnik, and M. Ottolenghi, *ibid.*, **76**, 1133 (1972).

[8] C. Pac and H. Sakurai, *Tetrahedron Lett.*, 3829 (1969); R. S. Davidson, *Chem. Commun.*, 1450 (1969).