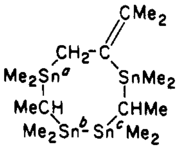
ca. 40% yield (^{119}Sn NMR), the main product being one in which one allene unit reacts with one tin–tin bond of the six-membered ring to give molecule 5. This structure



5

follows from the tin-119 NMR data, which are given in a footnote to Table I: most important is the presence of a one-bond tin–tin coupling, though it is surprising that the two tin nuclei b and c are isochronous.

A typical experimental procedure was as follows: 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane (5.51 g, 8.9 mmol) and 3-methyl-1-butyn-3-ol (1.64 g, 19.5 mmol) in xylene (10 mL) were heated for 15 h at 85 °C in the presence of 0.5 mol % tetrakis(triphenylphosphine)palladium(0), after which time the proton NMR spectrum indicated complete consumption of the tetrastannacyclohexane. The xylene and any low-boiling materials were removed at the water pump, leaving an oil that underwent sublimation to give a colorless solid (4.95 g, 73%), mp 53 °C. In all other cases, the reaction products were obtained as oils that were purified by Kugelrohr distillation. The methylenedistannacyclopentanes are extremely air sensitive, the distannacyclopentenes much less so.

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for supporting this work.

Registry No. 1a, 93061-62-2; **1b**, 93061-63-3; **1c**, 93061-64-4; **1d**, 93061-65-5; **1e**, 93061-66-6; **2a**, 93061-67-7; **2b**, 93061-68-8; **2c**, 93061-69-9; **5**, 93061-70-2; $HOMe_2CC{\equiv}CH$, 115-19-5; $MeOCOC{\equiv}CH$, 922-67-8; $Me_2NCH_2C{\equiv}CH$, 7223-38-3; $CH_2{=}C{=}CMe_2$, 598-25-4; 1,1,2,2,4,4,5,5-octamethyl-1,2,4,5-tetrastannacyclohexane, 89748-39-0; 1,1,2,2,3,4,4,5,5,6-decamethyl-1,2,4,5-tetrastannacyclohexane, 93061-71-3; 1,1,2,2,3,3,4,4,5,5,6,6-dodecamethyl-1,2,4,5-tetrastannacyclohexane, 93061-72-4; tetrakis(triphenylphosphine)palladium(0), 14221-01-3.

Supplementary Material Available: Tables of elemental analyses and ^{13}C NMR data (4 pages). Ordering information is given on any current masthead page.

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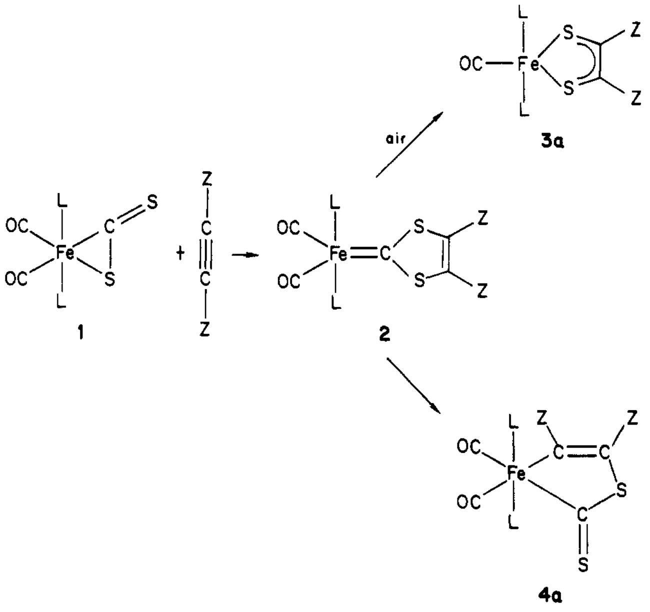
Summary: The new mixed bimetallic carbene complex $Cl_2HgFe(CS_2C_2(CO_2Me)_2)(CO)_2(PMe_2Ph)_2$ (**5**) has been obtained by addition of $HgCl_2$ to the reactive intermediate $Fe(CS_2C_2(CO_2Me)_2)(CO)_2(PMe_2Ph)_2$ (**2a**). The donor–acceptor adduct **5** has been characterized by single-crystal X-ray diffraction methods that establish the position of the $HgCl_2$ unit trans to the carbene ligand.

Scheme I



a, L = PMe₂Ph; Z = CO₂R

Eighteen-valence-electron transition-metal complexes, when they are basic enough, are known to form donor–acceptor adducts with Lewis acids such as HgX_2[1,2] or with 16-electron organometallic species.[3] Although these donor–acceptor compounds are well documented, to our knowledge they have not been made for the purpose of trapping unstable, 18-electron intermediates. Here we report that the formation of a metal→mercury(II) bond can be successfully used to stabilize an electron-rich, highly reactive metal–carbene complex.

We have already shown that the (1,3-dithiol-2-ylidene)iron intermediates **2** can be readily obtained by cycloaddition of activated alkynes to the η^2-CS_2 ligand of complexes **1**[4] (Scheme I). However, these electron-rich iron(0) complexes are very air-sensitive and decompose to give (dithiolene)iron derivatives **3**[5] and tetrathiafulvalenes.[5,6] Alternatively, when the phosphorus group L is a basic phosphine (L = PMe_2Ph, PMe_3), they rapidly isomerize into stable metallocyclic iron(II) complexes **4**[4] (Scheme I). Consequently, we were not able to characterize structurally an iron–carbene complex of type **2**. We now show that the intermediate **2a** reacts with $HgCl_2$ to give a crystalline adduct and that the formation of the Fe→$HgCl_2$ bond, in the position trans to the carbene ligand, prevents the transformation of the adduct into complex **3a** or **4a** and allows the X-ray structure determination of the first carbene iron–mercury(II) complex.

The yellow solution of 0.43 mmol (0.20 g) of **1a** (L = PMe_2Ph), in 40 mL of anhydrous ether, was stirred with 1 equiv of dimethyl acetylenedicarboxylate at room temperature under an inert atmosphere. After a few minutes, 1 equiv (0.45 mmol, 0.13 g) of $HgCl_2$ was added to the

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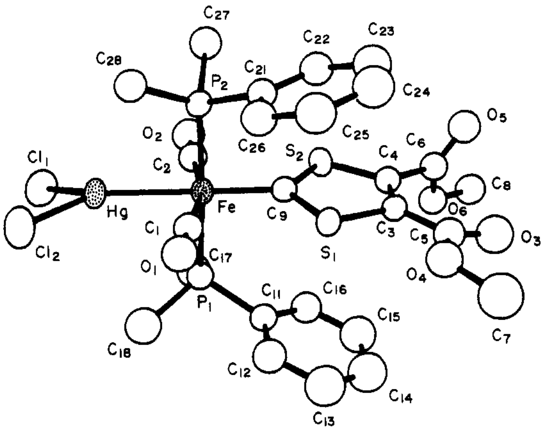
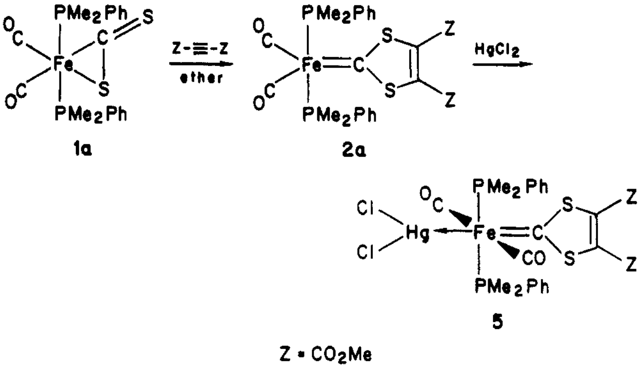


Figure 1. View of $Cl_2HgFe(CO)_2(PMe_2Ph)_2(CS_2C_2(CO_2Me)_2)$ (5). Important bond lengths (Å): Hg–Fe = 2.546 (1), Hg–Cl(1) = 2.486 (2), Hg–Cl(2) = 2.514 (2), Fe–P(1) = 2.282 (2), Fe–P(2) = 2.260 (2), Fe–C(1) = 1.761 (8), Fe–C(2) = 1.744 (8), Fe–C(9) = 1.912 (7), C(9)–S(1) = 1.688 (7), C(9)–S(2) = 1.704 (7), S(1)–C(3) = 1.743 (7), S(2)–C(4) = 1.739 (7), and C(3)–C(4) = 1.324 (9). Important bond angles (deg): P(1)–Fe–P(2) = 175.60 (8), C(1)–Fe–C(2) = 162.8 (3), Hg–Fe–C(9) = 176.5 (2), Hg–Fe–P(1) = 85.73 (6), Cl(1)–Hg–Cl(2) = 102.89 (2), Hg–Fe–Cl(1) = 132.86 (6), Hg–Fe–Cl(2) = 123.05 (7), Fe–C(9)–S(1) = 123.6 (4), Fe–C(9)–S(2) = 124.0 (4), and S(1)–C(9)–S(2) = 112.2 (4).

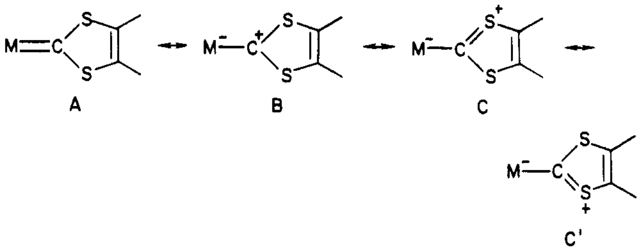
Scheme II



resulting brown solution of complex 2a [IR (C_6H_6) ν(CO) 1890, 1845 cm^{-1}][4] to afford a bright yellow precipitate, slightly soluble in ether. The precipitate was obtained in 82% yield, crystallized in methanol–ether, and identified to be the heterobimetallic carbene complex 5[7] (Scheme II). The remaining solution did not contain any tetrathiafulvalene or heterometallocycle 4. The infrared spectrum showed only one strong carbonyl absorption band at 1940 cm^{-1}, consistent with trans carbonyl ligands. The ^1H NMR spectrum[7] showed equivalent CO_2Me groups (3.92 ppm), indicating the retention of the symmetrical carbene moiety. The methyl groups and phosphorus nuclei of the PMe_2Ph ligands were also equivalent [^1H NMR[7] 2.10 ppm (d, PMe, $^2J_{PH}$ = 8 Hz); ^{31}P NMR[7] 21.87 ppm ($^2J_{^{31}P-^{199}Hg}$ = 742 Hz)]. These data are compatible with a plane and a C_{2v} axis of symmetry in the molecule. The value $^2J(^{31}P-^{199}Hg)$ appears to be a unique example of a coupling constant between ^{31}P and ^{199}Hg nuclei in the cis position.[2]

The stability of 5 in the solid state, in contrast to that of 2a, allowed the determination of its structure by an X-ray diffraction study.[8,9] An ORTEP diagram of the

Scheme III



molecule is shown in Figure 1. Complex 5 consists of a combination of the two $HgCl_2$ and $Fe(CO)_2(PMe_2Ph)_2$-$[CS_2C_2(CO_2Me)_2]$ moieties, with the Lewis acid ligand $HgCl_2$ in the position trans to the electron-releasing carbene ligand [Hg–Fe–C(9) = 176.5 (2)°]. Both the carbonyl and the phosphine ligands are trans to each other.

The Hg–Fe bond length (2.546 (1) Å) is similar to that in known Hg–Fe complexes containing different HgX_2 moieties such as in $Fe(CO)_4(HgClpy)_2$[10] (2.553 (8) Å), $[Fe(CO)_4(HgCl)(HgCl_2)]^-(AsPh_4)^+$[11] [2.560 (3) and 2.516 (4) Å], or $Hg[Fe(CO)_2(NO)PEt_3]_2$[12] (2.534 (2) Å). The Hg atom is 0.157 Å out of the plane [Cl(1),Cl(2),Fe] and the [Cl(1)Cl(2)Hg][FeC(1)C(2)C(9)] dihedral angle is 18.2°. The two Hg–Cl bond lengths are similar, but the Cl–Hg–Fe angles are significantly different.

The (carbene)C–Fe distance (1.912 (7) Å) is markedly shorter than in other monodentate carbene iron complexes:[13] 2.007 (5) Å in $(OC)_4Fe{=}\overline{CN(Me)CH_2CH_2N}Me$[14] and 1.979 (3) Å in $[Fe(C_7H_6)(CO)_2(C_5H_5)]PF_6$.[15] Of special interest is the cyclic carbene ligand itself which is roughly planar and has a C(3)═C(4) double bond (1.324 (9) Å). The carbon–sulfur bond distances [C(9)–S(1) = 1.688 (7) Å and C(9)–S(2) = 1.704 (7) Å] are significantly shorter than (i) the expected C(sp^2)–S single-bond length 1.79 Å), (ii) the corresponding C–S distances in the same carbene group bonded to manganese in $Mn(CS_2C_2(CO_2Me)_2)(CO)(P(OMe)_3)(C_5H_5)$[16] (av 1.74 Å), and (iii) the (olefinic)C–S bond lengths in 5 [C(3)–S(1) = 1.743 (7) Å; C(4)–S(2) = 1.739 (7) Å]. This suggests that the coordination of $HgCl_2$ to the iron atom decreases the Fe–carbene back-donation and induces an important electron transfer from the sulfur atoms of the cyclic carbene group toward the metal atom. Alternatively, if we consider the possible canonical forms A ↔ B ↔ C for a Fischer-type metal carbene complex (Scheme III), the formation of the Fe–Hg(II) bond in 5 strongly favors an average of the canonical forms C and C′.

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[7] 5: IR (Nujol) ν(CO) 1940 (s), ν(C═O) 1740 (s), ν(C═C) 1560 (w) cm^{-1}; ^1H NMR (60 MHz, 300 K, CD_2Cl_2) δ 7.40 (m, C_6H_5), 3.92 (s, OMe), 2.10 (s, PMe, $^2J_{PH}$ = 8 Hz); ^{31}P NMR (32.38 MHz, 309 K, CD_2Cl_2) signal at 21.87 ppm constituted of a singlet and of a symmetrical doublet ($^2J_{^{31}P-^{199}Hg}$ = 742 Hz) in the ratio s/d = 84/16. Anal. Calcd for $C_{25}H_{28}Cl_2O_6P_2S_2HgFe\cdot{}^1/_4Et_2O$: C, 34.82; H, 3.41; Cl, 7.90; P, 6.92; S, 7.14. Found: C, 34.96; H, 3.45; Cl, 7.32; P, 6.09; S, 6.62.

[8] Single crystals of 5 ($HgFeCl_2S_2P_2O_6C_{25}H_{28}$) were grown by diffusion of ether into a methanol solution of the complex. They belong to the space group $C2/c$, No. 15: M_r = 877.9, a = 35.059 (5) Å, b = 11.706 (1) Å, c = 17.600 (2) Å, α = 90.00°, β = 101.96 (1)°, γ = 90.00°, U = 7067 (3) Å^3, D_{calcd} = 1.65 g·cm^{-3}, Z = 8, λ (Mo Kα) = 0.71069 Å, μ(Mo Kα) = 12.3 cm^{-1}. The structure was solved by a combination of direct methods and difference Fourier techniques.[9] The final R factor based on 5250 observed reflections was 0.044.

[9] Diffraction data were collected on an Enraf-Nonius CAD-4 automatic diffractometer. All calculations were done on a Digital Equipment Corp. PDP 11/45 Computer using the Enraf-Nonius SDP program library.

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The simple formation of the donor-acceptor Fe-Hg adducts, such as **5**, may open a new method for the stabilization of other electron-rich, 18-electron metal complexes.

Supplementary Material Available: Tables of crystallographic data, interatomic distances and angles, final positional and thermal parameters, and structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Cobalt Complexes of Hexafluorodehydrocyclooctatetraene: Synthesis and Crystal and Molecular Structures of $[Co(CO)_3]_2(C_8F_6)$ and $[Co(CO)_2(PPh_3)]_2(C_8F_6)$

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Summary: While octafluorocyclooctatetraene (OFCOT) reacts with $[Co(CO)_4]^-$ to afford low yields of a dinuclear complex **1**, shown by X-ray diffraction studies to contain a severely puckered hexafluorodehydrocyclooctatetraene ring, reaction with $[Co(CO)_3(PPh_3)]^-$ yields a dinuclear analogue **2**, shown by X-ray diffraction to contain an almost planar C_8F_8 ring sandwiched between phenyl rings of adjacent triphenylphosphine ligands and a mononuclear complex **3**. Dinuclear **2** is shown not to arise by fluoride displacement from mononuclear **3**, but OFCOT reacts with $[Fe(C_5H_5)(CO)_2]^-$ by a consecutive displacement mechanism to afford initially the mononuclear complex **4** and subsequently the dinuclear complex **5**, which contains a 1,5-disubstituted cyclooctatetraene ring.

The nonplanar ground-state structure of cyclooctatetraene and its derivatives is well established,[4] and the molecular structure of octafluorocyclooctatetraene (OFCOT) has been shown to resemble closely that of its hydrocarbon analogue.[5] There has been considerable interest in whether the corresponding dehydro[8]annulenes (cyclooctatrienynes) are planar or puckered;[6] low-temperature X-ray diffraction studies of the highly reactive 5,6-didehydrodibenzo[*a*,*e*]cyclooctene show it to have a planar eight-membered ring.[7] In a previous communication[8] we reported the serendipitous synthesis of a compound $[Co(CO)_3]_2(C_8F_6)$, **1**, whose spectroscopic properties suggested the presence of a metal-stabilized hexafluorodehydrocyclooctatetraene ring. Here we report details of an X-ray crystallographic study of **1** which shows that the C_8F_6 ring is severely puckered, and the synthesis and X-ray diffraction study of a bis(triphenylphosphine) derivative, **2**, in which the C_8F_6 ring is almost planar.

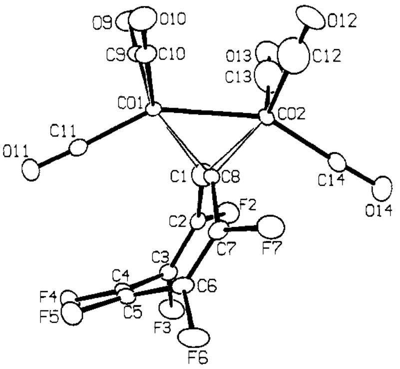


Figure 1. ORTEP drawing of the structure of 1, showing 30% equiprobability ellipsoids.

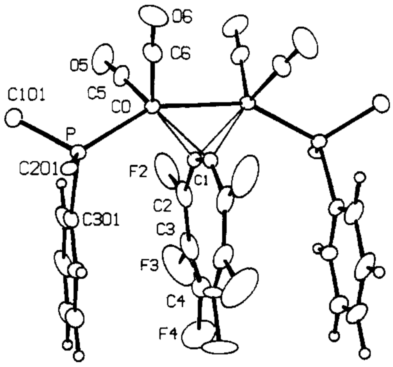
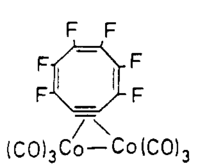
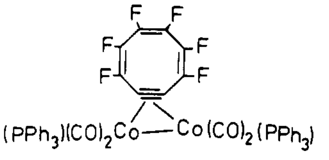


Figure 2. ORTEP drawing of the structure of 2, showing 30% equiprobability ellipsoids for non-hydrogen atoms. Phenyl carbons are numbered C101-C106, C201-C206, and C301-C306. The phenyl rings that sandwich the C_8F_6 ring are shown; for the other phenyl rings, only the C atoms bonded to P are shown.



1



2

Compound **1** was prepared in low yield by the reaction of OFCOT with $[Co(CO)_4]^-$ as described previously.[8] The bis(triphenylphosphine) derivative **2**[9] was prepared in higher yield by the reaction of OFCOT with the $[Co(CO)_3(PPh_3)]^-$ anion in THF at 20 °C; a second product of this reaction was the mononuclear complex **3**.[10] Compound **2** was also obtained by direct reaction of OFCOT with dinuclear $[Co(CO)_3(PPh_3)]_2$ in refluxing benzene; no **3** was detected in this reaction and no reaction occurred between these substrates at room temperature. Notably, reaction of pure **3** with a further equivalent of $[Co(CO)_3(PPh_3)]^-$ yielded no trace of **2**. In contrast, treatment of the mononuclear iron complex **4**[8] with excess $[Fe(C_5$-

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(9) Compound 2: 25% mp 182-185 °C; IR (CH_2Cl_2) ν_{CO} 2046 (s), 2002 (m), 1995 (m) cm^{-1}; mass spectrum, *m/e* 964 (P^+); ^{19}F NMR ($CDCl_3$, shifts in ppm upfield from internal $CFCl_3$) 104.0 (m, 2 F), 138.3 (m, 2 F), 142.7 (m, 2 F). Satisfactory microanalysis results have been obtained for all compounds reported here.

(10) Compound 3: 14%; mp 119-122 °C dec; IR (hexanes) ν_{CO} 2062 (m), 1990 (vs) cm^{-1}; ^{19}F NMR ($CDCl_3$, shifts in ppm upfield from internal $CFCl_3$) 73.4, 94.5, 120.2, 125.0, 128.7, 130.9, 142.2 (all multiplets, each having relative intensity = 1 F). See ref 8 for NMR data for analogues of 3.

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