Table X. Binding Energies for Clusters[a]

cluster	symmetry	BE/atom	
		REX	EHT
Ge_9^{4-}	C_{4v}	1.81	2.08
Ge_9^{2-}	D_{3h}	1.88	2.17
Sn_4^{2-}	D_{2d}	2.28	2.90
Sn_5^{2-}	D_{3h}	2.02	2.70
Sn_9^{4-}	C_{4v}	2.02	2.65
Sn_9^{2-} [b]	C_{4v}	2.00	2.62
Pb_5^{2-}	D_{3h}	1.14	2.77
Pb_9^{4-}	C_{4v}	1.25	2.85
Pb_9^{2-} [b]	C_{4v}	1.20	2.80
Bi_4^{0} [c]	T_d	1.48	3.13
Bi_4^{2-} [c]	D_{4h}	1.40	2.85
Bi_9^{5+}	D_{3h}	1.49	3.45
Bi_9^{7+} [b]	D_{3h}	1.33	3.39

[a] BE/atom for $A_n^{q-} \equiv (1/n)[qE(A^-) + (n-q)E(A^0) - E(A_n^{q-})]$, in eV; BE/atom for A_n^{q+} given similarly, with $E(A^+)$ replacing $E(A^-)$. [b] Unknown species. [c] Reference 27.

$Bi_4^0(T_d)$ and $Bi_4^{2-}(D_{4h})$. We note a nearly constant value for all clusters of a given element, although Sn_4^{2-} is especially stable, while Bi_4^{2-} with its slightly antibonding excess electrons is comparatively less stable. Oxidized clusters such as the unknown Pb_9^{2-} and Bi_9^{7+} are also comparatively less stable. Of particular note is the fact that the use of the relativistic parameterization decreases the BE/atom for a given cluster; the percentage decreases from the larger EHT values are approximately 13%, 24%, 56%, and 57% for clusters of Ge, Sn, Pb, and Bi, respectively. This relativistic weakening of homopolar bonds, which we have previously noted,[27] reflects a tendency toward inertness for groups 4B and 5B with increasing atomic number. Similar effects for other groups have been discussed in recent reviews[46,47] and in effective potential studies[48] of Tl_2. By contrast, Hartree–Fock–Slater studies[49] of Au_2 and Hg_2^{2+} as compared to those of Ag_2 and Cd_2^{2+} indicate a relativistic strengthening of bonds for these *ns* and ns^2 elements.

VI. Summary

In this present installment of our series of investigations of the effects of relativity on chemical bonding and structure, we have applied the REX method to the study of a number of charged clusters of Ge, Sn, Pb, and Bi atoms. Particular emphasis has been placed on the properties of both homonuclear and heteronuclear nine-atom clusters. These properties include structural rearrangement energies, charge distributions, and binding energies. The example of substitutional site preferences for heteroatoms is used to introduce a more general discussion of the role of relativity in modifying the variation of atomic electronegativities with atomic charge. Some predictions are made concerning the expected electronic absorption spectra of many of the complexes.

Acknowledgment. We wish to thank Professor R. W. Rudolph (deceased) for many valuable discussions about these heavy-element clusters and for permission to quote some results of his ^{119}Sn NMR investigations prior to publication. We also wish to thank the University of Michigan Computing Center for the use of its facilities.

Registry No. Ge_9^{4-}, 59457-98-6; Ge_9^{2-}, 64826-71-7; Sn_4^{2-}, 78413-16-8; Sn_5^{2-}, 61583-40-2; Sn_9^{4-}, 12597-40-9; Pb_5^{2-}, 58798-64-4; Pb_9^{4-}, 67417-86-1; Bi_9^{5+}, 39448-36-7; $SnGe_8^{4-}$, 76845-90-4; $GeSn_8^{4-}$, 76845-83-5; $PbSn_8^{4-}$, 67660-32-6; $TlSn_8^{5-}$, 76845-91-5; $PbSn_4^{2-}$, 78987-31-2; Sn_9^{2-}, 79068-86-3; Pb_9^{2-}, 79068-85-2; Bi_9^{7+}, 79068-84-1; $TlSn_8^{3-}$, 78987-32-3.

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Molecular Systematics in Metal Tetrathiolenes. A Novel 2-, 4-, 6-, 8-, and 12-Electron-Donating Ligand System upon Coordination to One, Two, Two, Three, and Four Metals, Respectively

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Received March 18, 1981

New synthetic and structural evidence has led to a unified pattern of the versatile coordination chemistry of the tetrathiolene ligands: tetrathionaphthalene (TTN, $C_{10}H_4S_4$), tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$), and tetrathiotetracene (TTT, $C_{18}H_8S_4$). These ligands can act as, formally, 2-, 4-, 6-, 8-, and 12-electron (*n*e) donors (assumed to be neutral) when coordinated to one, two, two, three, and four metals, respectively. Molecular designs via electronic, steric, and reactivity controls give rise to an unusual array of novel metal tetrathiolene complexes or clusters. This paper reports the preparations, characterization, and chemical and physical properties of the following novel systems: (a) 2e systems, $(Ph_3P)_2(CO)XIr(TCTTN)$ where X = Cl, H; (b) 4e systems, $(Ph_3P)_4Pt_2(TTN)$ (reported elsewhere); (c) 6e systems, $(Ph_3P)_2(CO)_2I_2Ir_2(TCTTN)$; (d) 8e systems, $(Ph_3P)_2Pt(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$; (e) 12e systems, $(Ph_3P)_2(CO)_2H_2Ir_2(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$. Single-crystal X-ray structural determinations revealed that the 2e systems $(Ph_3P)_2(CO)XIr(TCTTN)$ have an octahedrally coordinated iridium with two triphenylphosphines in a trans configuration and an equatorial plane containing two sulfur atoms from TCTTN, the carbonyl group, and the X atom; the molecule as a whole, however, deviates significantly from planarity. High-pressure liquid chromatography using gel permeation was used to help separate and identify the products.

Recently we reported the preparations and structures of two distinctly different bimetallic complexes $(Ph_3P)_4Pt_2(TTN)$[1] and $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)$[2] based on the tetrathiolene (TTL) ligands:[1-6] tetrathionaphthalene (TTN, $C_{10}H_4S_4$),[7] tetrachlorotetrathionaphthalene (TCTTN, $C_{10}Cl_4S_4$),[8] and

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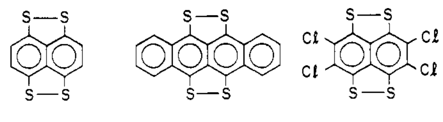
Chart I



TTN TTT TCTTN

tetrathiotetracene (TTT, $C_{18}H_8S_4$).[9] These ligands (cf. Chart I) possess three attractive features which make this class of organic compounds excellent ligands in metal–organic chemistry. First, they are strictly planar with extensive π-electron delocalization. Second, each of these molecules has two S–S bonds, one on each side of the molecule, suitable for oxidative addition(s) to low-valent transition-metal complexes. And, finally, upon coordinating to two metal complexes, each of these ligands presumably can accommodate up to a total of four (formal) electrons. The implication of such a qualitative consideration is that the resulting complexes will undergo facile redox reactions. Indeed, the rich electrochemistry of these complexes has been verified experimentally.[3,4] In analogy to the well-known metal–dithiolene systems, these complexes can be named as metal tetrathiolenes (TTL) or metal tetrathienes.

It now occurs to us that these bimetallic complexes are just two members of a novel series of metal tetrathiolene complexes. We report herein the syntheses and characterizations of first examples of the corresponding mono-, tri-, and tetrametal complexes: $(Ph_3P)_2(CO)XIr(TCTTN)$, where X = Cl, H, $(Ph_3P)_2Pt(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$, and $(Ph_3P)_2(CO)_2H_2Ir_2(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$, respectively. These five classes of compounds constitute a unified pattern of metal tetrathiolene coordination chemistry. Simple electron bookkeeping reveals that the ligand acts as, formally, a 2-, 4-, 6-, 8-, and 12-electron donor when coordinated to one, two, two, three, and four metals, respectively. This unique coordination chemistry stems from the electronic, steric, and reactivity properties of the ligands as well as that of the metals. While purifications of these compounds are often carried out by repeated recrystallization, we show here that high-pressure liquid chromatography (HPLC) can be used effectively to separate and identify the products.

Experimental Section

All preparations were performed in an argon-filled Vacuum Atmospheres drybox. Reagent grade benzene, methylene chloride, and acetonitrile were freshly distilled from CaH_2, P_2O_5, and CaH_2, respectively, under nitrogen. Infrared (IR) spectra (4000–250 cm^{-1}) were recorded as CsI pellets prepared in the drybox with a Perkin-Elmer Model 467 grating spectrophotometer. UV–vis spectra (800–190 nm) were recorded in degassed Spectrograde DMF or CH_2Cl_2 (Eastman Organic Chemicals) solutions in quartz cells with a Varian Model 634S spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, and Schwarzkopf Microanalytical Laboratory, Woodside, NY.

The ligand TCTTN was prepared according to the literature method.[8] The only modification was Soxhlet extraction using CS_2 as solvent in the final recrystallization. $Pt(PPh_3)_4$, $IrHCl(CO)(PPh_3)_3$, and Vaska's compounds were purchased from Strem Chemicals. The identity of these starting materials was checked by infrared spectroscopy and/or elemental analysis.

Preparations and Characterizations. Figure 1 summarizes the reactions, structures, and examples of these novel metal tetrathiolenes.

The new 2e system $(Ph_3P)_2(CO)ClIr(TCTTN)$ (**1a**) was prepared by the following procedure. A mixture containing 1 mmol of TCTTN and 1 mmol of PPh_3 in 20 mL of benzene was heated to reflux under constant stirring. To this was added 1 mmol of $IrCl(CO)(PPh_3)_2$ in 45 mL of benzene over a period of 3 h. The resulting dark red solution was refluxed overnight. The volume of the reaction mixture was reduced by ca. two-thirds, and a threefold excess of CH_3CN was added to precipitate the orange-red product. The major impurity in the crude product is the diiridium species $(Ph_3P)_2(CO)_2Cl_2Ir_2(TCTTN)$ (which was minimized by adding 1 equiv of PPh_3 to the reaction mixture) and TCTTN. Analytically pure samples can be obtained by first digesting the crude product with CH_2Cl_2 followed by recrystallization of the residue with benzene/CH_3CN. Anal. Calcd for $C_{47}H_{30}P_2S_4Cl_5IrO$ (**1a**): C, 48.62; H, 2.60; P, 5.34; S, 11.08; Cl, 15.28; Ir, 15.70. Found: C, 48.70; H, 2.92; P, 4.51; S, 12.48; Cl, 15.48; Ir, 15.86. IR (cm^{-1}): ν_{CO}, 2052 (strong). UV–vis (λ_{max} in nm with ϵ in M^{-1} cm^{-1} in parentheses, in CH_2Cl_2): 467 (9.28×10^3), 428 (sh, 1.11×10^4), 398 (9.91×10^3), 360 (sh, 7.23×10^3), 285 (sh, 2.94×10^4), 273 (3.44×10^4), 248 (sh, 4.29×10^4). $(Ph_3P)_2(CO)HIr(TCTTN)$ (**1b**) was prepared by refluxing a mixture of 1 mmol of $IrH(CO)(PPh_3)_3$ and 1 mmol of TCTTN in 25 mL of benzene for 24 h. To the resulting red solution was added an equal volume of CH_3CN. The bright orange product was filtered and recrystallized from CH_2Cl_2/CH_3CN. Anal. Calcd for $C_{47}H_{31}P_2S_4Cl_4IrO$ (**1b**): C, 49.69; H, 2.75; P, 5.45; S, 11.29; Cl, 12.48. Found: C, 50.01; H, 3.51; P, 5.16; S, 10.79; Cl, 13.17. IR (cm^{-1}): ν_{CO} 2026 (strong), ν_{IrH} 2037 (sharp shoulder). UV–vis (nm, M^{-1} cm^{-1}, CH_2Cl_2): 460 (1.34×10^4), 430 (sh, 1.07×10^4), 363 (6.82×10^3), 265 (4.18×10^4).

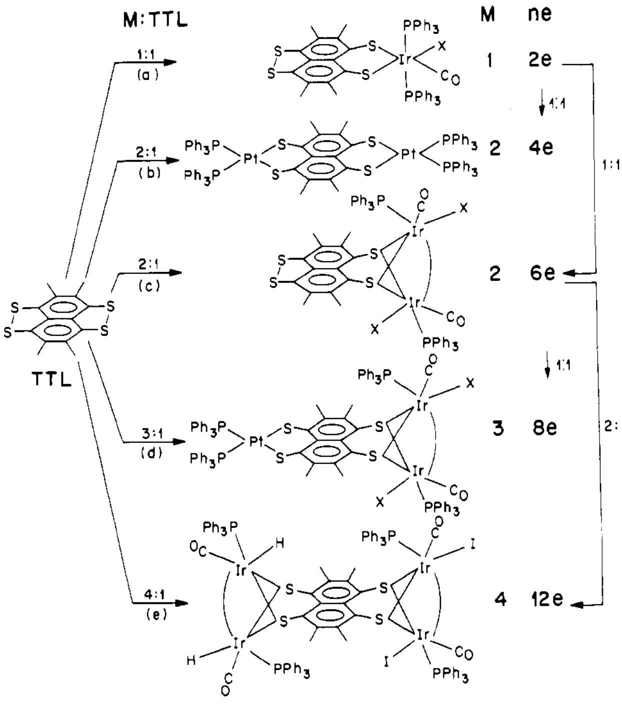


Figure 1. Structures, reactions, and some illustrative examples of metal tetrathiolenes (TTL) containing one, two, two, three, and four metals (M) which correspond to 2-, 4-, 6-, 8-, and 12-electron (*n*e) systems, respectively: (a) 2e systems, $(Ph_3P)_2(CO)XIr(TCTTN)$ where X = Cl (**1a**), H (**1b**); (b) 4e systems, $(Ph_3P)_4Pt_2(TTN)$ (**2a**); (c) 6e systems, $(Ph_3P)_2(CO)_2X_2Ir_2(TTL)$ where X = Br and TTL = TTN (**2b**), X = I and TTL = TCTTN (**2c**); (d) 8e systems, $(Ph_3P)_2Pt(TCTTN)Ir_2I_2(CO)_2(PPh)_2$ (**3**); (e) 12e systems, $(Ph_3P)_2(CO)_2H_2Ir_2(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$ (**4**).

The preparations and the structures of 4e system $(Ph_3P)_4Pt_2(TTN)$ (**2a**)[1] and the 6e system $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)$ (**2b**)[2] have been reported elsewhere.

We have also prepared the 6e systems $(Ph_3P)_2(CO)_2X_2Ir_2(TCTTN)$ where X = H, Cl, Br, and I (**2c**). Since **2c** will be used as starting material in the preparations of the 8e and 12e systems to be described next, we include the results of elemental analysis and spectroscopic characterizations as follows. $(Ph_3P)_2(CO)_2I_2Ir_2(TCTTN)$ (**2c**). Calcd for $C_{48}H_{30}P_2S_4Cl_4I_2Ir_2O_2$: C, 35.83; H, 1.88; P, 3.85; S, 7.97; Cl, 8.81; I, 15.77; Ir, 23.89. Found: C, 35.91; H, 2.00; P, 3.84; S, 9.11; Cl, 8.88; I, 15.07; Ir, 23.06. IR (cm^{-1}): ν_{CO}, 2014, 2022 (strong). UV–vis (nm, M^{-1} cm^{-1}, CH_2Cl_2): 470 (sh, 2.34×10^4), 445 (2.49

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Table I. Retention Times (Min) for Some Metal Tetrathiolenes Obtained with Gel Permeation Chromatography[a, b]

	compd	retention time
I	$Ir(H)(CO)(Ph_3P)_2TCTTN$	18.0
II	$Ir_2(Cl)_2(CO)_2(Ph_3P)_2TCTTN$	16.9[c] 17.9[c]
III	$Ir_2(Br)_2(CO)_2(Ph_3P)_2TCTTN$	17.0
IV	$Ir_2(I)_2(CO)_2(Ph_3P)_2TCTTN$	17.4
V	$Ir_2(I)_2(CO)_2(Ph_3P)_2TCTTNPt(Ph_3P)_2$	15.8

[a] Four columns of μ-styragel, two each of 500-Å and 100-Å pore sizes; flow rate 2 mL/min; methylene chloride as solvent. All solid samples are dissolved in eluting solvent and filtered, with Waters Associates Sample Clarification Kit, before injection. [b] The retention time for benzene, which corresponds approximately to the column volume, is 23.0 min. The retention times for Ph_3P and TCTTN are 20.0 and 20.8 min, respectively. [c] Approximately equal intensities.

× 10^4), 389 (1.74 × 10^4), 290 (3.40 × 10^4).

The new trimetallic 8e system $(Ph_3P)_2Pt(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$ (**3**) was prepared by reacting **2c** (1 mmol) with a stoichiometric amount of $Pt(PPh_3)_4$ in 25 mL of benzene at room temperature. The bright red microcrystalline precipitate formed was filtered, washed with acetonitrile, and recrystallized from CH_2Cl_2/CH_3CN. Anal. Calcd for $C_{84}H_{60}P_4S_4Cl_4I_2Ir_2PtO_2$ (**3**): C, 43.33; H, 2.60; P, 5.32; S, 5.51; Cl, 6.09; I, 10.90; Pt, 8.38. Found: C, 43.80; H, 2.98; P, 5.30; S, 5.71; Cl, 5.71; I, 10.63; Pt, 7.87. IR (cm^{-1}): ν_{CO} 2008 (strong). UV-vis (nm, M^{-1} cm^{-1}, CH_2Cl_2): 530 (2.34 × 10^4), 500 (sh, 1.94 × 10^4), 425 (sh, 1.50 × 10^4), 375 (2.22 × 10^4), 275 (sh, 6.70 × 10^4).

The new tetrametallic 12e system $(Ph_3P)_2(CO)_2H_2Ir_2(TCTTN)Ir_2I_2(CO)_2(PPh_3)_2$ (**4**) was prepared by refluxing a 1:2 mixture of **2c** and $IrH(CO)(PPh_3)_3$ in benzene for 24 hs. The volume of the resulting dark red solution was reduced by ca. two-thirds and a threefold excess of CH_3CN added. The resulting red-brown microcrystalline product was filtered, washed with CH_3CN, and recrystallized from CH_2Cl_2/CH_3CN. Anal. Calcd for $C_{86}H_{62}P_4S_4Cl_4I_2Ir_4O_4$ (**4**): C, 40.10; H, 2.42; P, 4.81; S, 4.98. Found: C, 39.74; H, 3.13; P, 5.90; S, 5.63. IR (cm^{-1}): ν_{CO} 1975 (strong), ν_{IrH} 2004 (sharp). UV-Vis (nm, M^{-1} cm^{-1}, CH_2Cl_2): 590 (4.51 × 10^3), 475 (2.21 × 10^4), 399 (2.37 × 10^4), 332 (4.35 × 10^4), 290 (sh, 5.39 × 10^4).

High-Pressure Liquid Chromatography. The high-pressure liquid chromatographic system used was a combination of Waters Associates Model 6000A solvent delivery system, Model UK6 injector system, Model 440 Absorbance Detector, operating at 254 nm, and Model R401 Differential Refractometer detector. A Houston Instrument dual-pen Omniscribe was used to record the chromatograms.

The eluting solvent, methylene chloride, was purchased from Burdick & Jackson. The solvent was filtered with a 0.45 μm Teflon filter as part of a Millipore system purchased from Waters Associates and degassed under vacuum prior to use. The flow rate was set at 2 mL/min. The columns used were a set of four Waters Associates μ-styragel columns (7 mm i.d. × 30 cm) with two columns each of 500- and 100-Å pore sizes. Hamilton syringes (801 and 805) were used to inject the samples (5–150 μL) into the injector.

All samples were prepared immediately before use by filtering saturated solutions with a Waters Associates sample clarification kit in order to obtain solutions of the optimum concentration due to the low solubilities of most of the compounds reported here. The retention times for some representative compounds as well as their starting materials are listed in Table I.

Results and Discussions

Figure 1 summarizes the reactions, structures, and examples of the novel series of metal tetrathiolene complexes where the ligand acts as, formally, a 2-, 4-, 6-, 8-, and 12-electron donor when coordinated to one, two, two, three, and four metals, respectively.

Electron Counting Scheme. The simple electron counting scheme is exemplified in Figure 2. If we regard the coordinated TTL ligand as a neutral moiety, it can be seen that each of the four sulfur atoms can function as, formally, a one-electron donor, giving rise to a covalent metal–sulfur bond, or a three-electron donor bridging two metal atoms. In the bridging mode, the sulfur atom can be visualized as forming a second metal–sulfur "dative" bond via its lone electron pair. (It must be emphasized, however, that the two metal–sulfur bonds are more often than not equivalent). If we denote the number of nonbridging (monodentate) and bridging (bidentate) sulfur atoms by a and b, respectively, we can write eq 1 and 2 where $(a + b) \leq 4$ and n is the total number of

$$n = a + 3b \qquad (1)$$

$$M = b + a/2 \qquad (2)$$

electrons donated by the neutral TTL ligand to a total of M metal atoms. It is readily apparent that each system is completely characterized by two variables, n and M, or, conversely, a and b which are given by eq 3 and 4.

$$a = 6M - 2n \qquad (3)$$

$$b = n - 2M \qquad (4)$$

The total formal charge accumulated on the TTL ligand is simply $q- = (a + b)-$. For example, the TTL ligands of the 4e, 8e, and 12e systems are all fully reduced with a formal charge of 4– (cf. Chart II). In going from 4e to 8e to 12e, the lone pairs of the sulfur atoms (two per two sulfurs) become coordinated to the incoming metal atom(s). In contrast, the TTL ligands of 2e and 6e systems are half-reduced corresponding to a formal charge of 2– (cf. Chart II). Again, in going from 2e to 6e, the two lone pairs on the two "coordinated" sulfur atoms become coordinated to the second metal atom.

An alternative, equally viable, electron-counting scheme is based on anionic rather than neutral TTL ligands. If one considers the TTL ligand in the n = 2, 4, 6, 8, and 12e systems

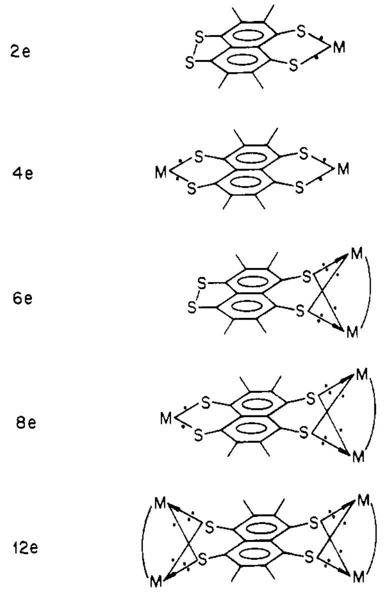


Figure 2. Schematic representations of the electron bookkeeping scheme for metal tetrathiolenes containing one, two, two, three, and four metals (M), corresponding to 2-, 4-, 6-, 8-, and 12-electron (ne) systems, respectively.

Chart II

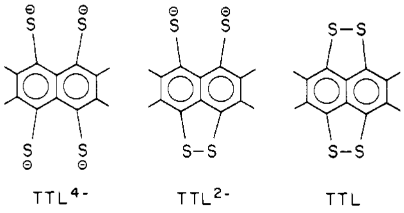
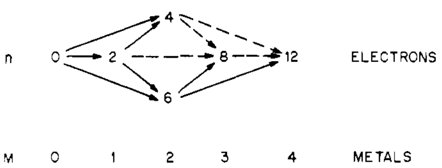


Chart III



as bearing formal charges of $q- = 2-, 4-, 2-, 4-$, and $4-$, these systems can be characterized as $n + q = 4, 8, 8, 12$, and 16e donors, respectively. In this way, $n + q = 4M$ since each metal has two metal–sulfur bonds and each metal–sulfur bond involves two electrons. Throughout this paper, however, we prefer to adopt the n rather than the $n + q$ electron-counting scheme.

Preparative Considerations. The preparations of some representative members of each class of metal tetrathiolenes are summarized in Figure 1 and described in detail in the Experimental Section. It is apparent that some of the *n*e systems can be prepared by direct reaction of the TTL ligands with metal complexes in stoichiometric ratios (TTL:M = 1:1, 1:2, 1:3, and 1:4 for $n = 2, 4, 6, 8$, and 12) while others may be more conveniently derived from some precursors with lower n values. For example, the 8e system can more conveniently be prepared from a 6e system via reaction with 1 equiv of a second metal complex (reaction scheme adopted here) rather than from a 2e system via reaction with 2 equiv of a second metal or from the ligand directly. Chart III summarizes the various reaction pathways for the preparation of the metal tetrathiolene systems discovered so far. The solid arrows represent the pathways known to date while the dashed arrows represent conceivable pathways.

Purification Methods. While preparations of these metal tetrathiolene complexes usually pose no great difficulty, the purification is often not straightforward due to various possible reaction products formed. The tedious process of repeated recrystallizations based on the solubility differences of the complexes in a variety of solvents have been used successfully to provide analytically pure compounds. We now find that high-pressure liquid chromatography (HPLC) can be very helpful in identifying the various reaction products and/or isomers as well as in separating the products from the starting materials and/or impurities. Here we use the method of size exclusion (gel permeation, GPC) and show that the present series of metal tetrathiolene complexes can be separated from one another and from their respective starting materials according to their effective molecular sizes.

Table I also shows the variation in retention times of a representative series of metal tetrathiolene complexes containing one to three metal atoms. The usefulness of the method of GPC is illustrated quite well in that small molecules have the longer retention times. The small solvent molecules such as benzene have the longest retention time of 23.0 min, corresponding approximately to the column volume. The mono-, di-, and triiridium complexes listed in Table I have retention times of ca. 18, 17–18, and 16 min, respectively, consistent with the increasing molecular sizes.

A more interesting result occurred when an analytically pure recrystallized sample of the dimetal species $(Ph_3P)_2(CO)_2Cl_2Ir_2(TCTTN)$ was injected into the HPLC. The absorbance at 254 nm shows two distinct peaks in the chromatograph with slightly different retention times (cf. Table I), indicating two species of similar molecular size. In the crude product obtained from the reaction mixture, the carbonyl stretching frequency is split into two bands. Upon recrystallization via Soxhlet extraction under constant reflux for several days, the carbonyl frequency splits into six bands. A change in the intensity of the two peaks which appear in the chromatogram is also seen in going from crude to analytically pure product. In the crude product, the peak with the longer retention time is much more intense whereas in the analytically pure product, the intensities of the two peaks are almost equal. One possible explanation may come from intra- or intermolecular ligand (including the triphenylphosphines) scrambling under prolonged heating, thereby giving rise to isomers of slightly different effective molecular sizes.

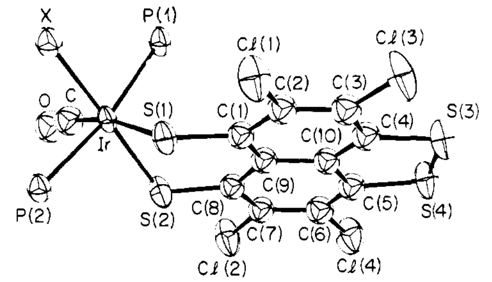


Figure 3. Structure of $(Ph_3P)_2(CO)XIr(C_{10}Cl_4S_4)$ where X = Cl (**1a**) and H (**1b**). Only nonphenyl nonhydrogen atoms are shown for clarity.

Metal Complexes as Ligands. It is important to point out that metal tetrathiolene *complexes* with an electron count of n can serve as potential *ligands* in the preparation of metal tetrathiolenes with an electron count of $n' > n$ provided that the n and M values satisfy eq 1 and 2. In fact, eq 3 and 4 indicate readily changes in the bonding mode of the sulfur atoms (a and b) as well as the overall formal charge on the TTL ligand. For example, in going from a monometallic 2e system to a trimetallic 8e system, $a = 2$ remains unchanged while b changes from 0 to 2, resulting in a change of the overall charge from 2– to 4–. While the unusually rich coordination chemistry of these ligands is exemplified here by their platinum and iridium complexes, it should be noted that we have synthesized numerous metal tetrathiolene complexes involving various transition metals in the periodic table, which will be subjects of future publications.

Stereochemical Varieties. The structures of the metal tetrathiolene systems are shown schematically in Figure 1. Single-crystal X-ray diffraction studies have been performed on the 2e systems **1a** and **1b** in order to unambiguously define their stereochemistry.[10] As shown in Figure 3, the iridium atom in **1a** or **1b** is octahedrally coordinated with two triphenylphosphines (in a trans configuration), two sulfur atoms from the TCTTN ligand, one carbonyl, and one chloride (**1a**) or hydride (**1b**) ligand. The important features are: (1) the $IrS_2(CO)X$ plane is not coplanar with the TCTTN plane (a unique feature of metal tetrathiolene structures[1]); (2) the nonbonded S(1)···S(2) distance is 3.16 Å whereas the intact S(3)–S(4) bond length is 2.07 Å (these values are similar to those found in the 6e system $(Ph_3P)_2(CO)_2Br_2Ir_2(TTN)^2$).

It should be noted that the two new 2e systems reported here are not "trivial" products of the oxidative addition reactions. Since there are two S–S bonds rather than one, there is no a priori reason to believe that the reaction will stop at 2e rather than go all the way to 4e. In fact, we are as yet unable to make the 2e system $(Ph_3P)_2Pt(TTN)$. Conversely, we have not succeeded in making the 4e system $(Ph_3P)_2(CO)ClIr(TTN)IrCl(CO)(PPh_3)_2$. These are intriguing observations which we will try to rationalize later. Even with one S–S bond as in $C_{10}Cl_6S_2$, it is not always possible to make the "trivial" oxidative addition product $(Ph_3P)_2M(C_{10}Cl_6S_2)$. For example, the reaction of equimolar amounts of $C_{10}Cl_6S_2$, which has one S–S bond, with $Pd(PPh_3)_3$ or $Pt(PPh_3)_4$ produced $(Ph_3P)_2M(C_{10}Cl_6S_2)$ where M = Pd, Pt, whereas the corresponding reaction with $[Ni(cycloocta\text{-}1,5\text{-diene})_2]$ in the presence of

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PPh_3 led to $(Ph_3P)_3Ni_3(C_{10}Cl_6S_2)_3$.[11] In this context, the 2e system must be considered as an important member of the series.

The bimetallic structures are rather unusual. As we have reported earlier[1] and shown schematically in Figure 1, the diplatinum compound adopts structure **2a** which has one metal on each side of the TTN ligand whereas the diiridium complex exhibits structure **2b** which has two metals on one side and none on the other side. The diplatinum 4e system **2a** involves a tetrathionaphthalene (TTN) ligand bridging two bis(triphenylphosphine)platinum moieties via cleavage of both sulfur–sulfur bonds to form four platinum–sulfur bonds. Each platinum atom is therefore coordinated to two phosphorus (from two PPh_3 ligands) and two sulfur (from the TTN ligand) atoms in a "square-planar" configuration. The platinum coordination is very nearly planar. The bridging TTN ligand is also close to planarity (except, perhaps, the sulfur atoms). The molecule as a whole, however, is by no means planar. The molecular distortions from planarity can be characterized as a rotation of the sulfur atoms about the central carbon–carbon bond of the bridging ligand followed by a rotation of each of the two platinum coordination planes about the sulfur···sulfur edge, resulting in the dihedral angles of 12.6 and 38.4°, respectively. These remarkable distortions have been rationalized in terms of intramolecular angular constraints as well as steric requirements.

On the other hand, the diiridium 6e system **2c** consists of two iridium atoms bridged by two sulfur atoms from one end of the TTN ligand, leaving the other S–S bond intact. The nonbonded S···S distance is 3.086 (9) Å whereas the intact S–S bond length is 2.070 (11) Å; both are quite analogous to those found in the 2e systems **1a** and **1b**. The molecule also has a short Ir–Ir bond of 2.688 (2) Å with the metal–metal bond conceptually occupying the sixth coordination site of the highly distorted octahedral coordinations which include two sulfur atoms (from TCTTN), one carbonyl group, one Ph_3P group, and one iodine atom. The Ir–Ir bond distance is comparable to that of 2.673 (1) Å found in a related structure $[(MeO)_3P(CO)HIr(\mu\text{-S-}t\text{-Bu})]_2$,[12] which is, in terms of the disulfur-bridged diiridium core, structurally analogous to **2c** (but with higher symmetry). This stereochemistry can be rationalized as representing a rare case of electronic effect prevailing over the steric constraints; the molecule, instead of adopting a sterically more favorable 4e $(Ph_3P)(CO)IIrS_2C_{10}H_4S_2IrI(CO)(PPh_3)$ structure with both iridium atoms being five-coordinated 16-electron Ir(III), adopts an electronically more favorable 6e $(Ph_3P)_2(CO)_2I_2Ir_2S_2C_{10}H_4S_2$ structure with both iridium atoms being six-coordinated 18-electron (rather uncommon) Ir(II).

No structural data are as yet available for the trimetallic 8e and the tetrametallic 12e systems. However, the elemental analysis and spectroscopic evidence presented in the Experimental Section leave no doubt about the existence and identity of these new compounds.

Reactivity, Electronic, and Steric Factors. It is obvious that the metal tetrathiolene complexes reported in this paper are products of a novel reaction sequence (cf. Figure 1) which is apparently controlled (controllable) by reactivity and the electronic and steric requirements of the ligands as well as the metals. First, oxidative addition of the first S–S bond to a metal complex produces the 2e system (e.g., **1**) via cleavage of the S–S bond. Accumulation of negative charge on the ligand deactivates the second S–S bond toward further oxidative addition. The second metal atom has two reaction sites available for attack. If its reactivity outweighs the deactivation of the S–S bond, it will favor the sterically less hindered site and cleave the second S–S bond, giving rise to a 4e system such as **2a**. Otherwise, electronic factors such as metal–metal bond formation may favor the original reaction site (leaving the second S–S bond intact), giving rise to a 6e system such as **2b**. In the reaction of 1–2 mol of $IrX(CO)(PPh_3)_2$ with 1 mol of TCTTN, we obtained a mixture of 2e and 6e systems whose ratio depends upon, among other things, PPh_3 concentration. We can force the iridium system to go from 2e to 4e by introducing other ligands with steric constraints and/or coordination requirements. One example is the preparation of the 4e system $[(dppe)_2Ir(TCTTN)Ir(dppe)_2]^{2+}$ from the 2e system $[(TCTTN)Ir(dppe)_2]^+$ where dppe = $Ph_2PCH_2CH_2PPh_2$.[13] The significantly deactivated S–S bond in the 6e system (e.g., **2c**) can only be cleaved by a reactive metal complex such as $Pt(PPh_3)_4$ to give the 8e system (e.g., **3**). Finally, the 12e system can be obtained either by direct reaction of the ligand with metal complexes which are reactive and sterically favorable (such as $IrCl(CO)(PMe_3)_2$) in a 1:4 ratio[13] or from the 6e system by further reaction with Vaska-type compounds such as the preparation of **4** from **2c**.

In short, a TTL ligand can act as a bi-, tetra-, tetra-, hexa-, and octadentate ligand using (μ-TTL) and/or di(μ-S) bridges when coordinated to one, two, two, three, and four metal complexes, respectively. In each case, it functions as a 2-, 4-, 6-, 8-, and 12-electron-donating ligand, respectively. The intermediate values can also be attained by redox reactions[3,4] or more elaborate reaction schemes. For example, $(Ph_3P)_4Pt_2(TTN)$ can be oxidized reversibly in four one-electron steps.[3] Since the electrons come out of orbitals which contain substantial amount of tetrathiolene ligand character, the mono-, di-, tri-, and tetracations can be considered as, formally, 3, 2, 1, and 0e systems, respectively. On the other hand, it may be possible to prepare the 10e system via alkylation of the two "uncoordinated" sulfur atoms of 6e system, thereby forcing them to use their lone pairs in coordination with the incoming metal atom(s). Clearly, more synthetic, structural, bonding, and physical data are needed in order to fully understand the unique and versatile coordination chemistry of the tetrathiolene ligands.

Registry No. **1a**, 79084-75-6; **1b**, 79084-47-2; **2c**, 79084-48-3; **3**, 79084-49-4; **4**, 79084-50-7; $Ir_2(Cl)_2(CO)_2(Ph_3P)_2TCTTN$, 79084-51-8; $Ir_2(Br)_2(CO)_2(Ph_3P)_2TCTTN$, 71894-97-8; $IrCl(CO)(PPh_3)_2$, 15318-31-7; $IrH(CO)(PPh_3)_3$, 17250-25-8; $Pt(PPh_3)_4$, 14221-02-4.

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