were passed over the residual TiO_2 under pyrolytic conditions. With the exception of neopentyl alcohol, no significant dehydration was observed. Thus, our study differs from that reported earlier by Bradley.[3d] Since the latter was done under static vacuum, the alcohol formed underwent dehydration to generate water, which, in turn, caused hydrolysis of the M–OR bonds. As a result, an autocatalytic decomposition of the metal alkoxide ensued.

Table I summarizes our decomposition data. On the basis of these, the following conclusions may be drawn.

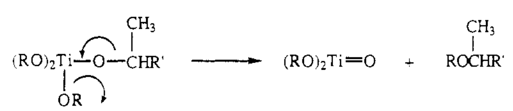
The complete absence of any products arising from the scission of the C_α--C_β bond rules out the formation of alkoxy radicals, RO•. This fragmentation mode is known to be particularly facile for tertiary and secondary alkoxy radicals.[8]

The pyrolysis of the cyclopropylcarbinyl alkoxide derivative, **5**, led to the formation of significant amounts of the ring-opened allylcarbinyl products. At the same time, no cyclobutyl derivative was observed. This product distribution supports at least the *transient* formation of the radical, R•[9] (eq 1) but argues against

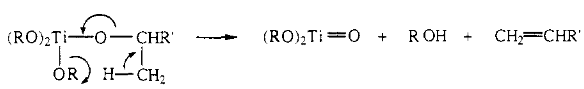
$$(RO)_3Ti{-}OR \rightleftharpoons [(RO)_3Ti{-}O\cdot \ \cdot R] \qquad (1)$$

the formation of the corresponding carbocation, R^+.[10] Also note that the formation of carbocation by charge separation in the gas phase is unlikely due to the absence of solvent stabilization of the charged species. However, *free* radicals *do not* appear to be the intermediates in the product formation since the pyrolysis of **4** did not yield dineopentane, neopentane, and/or 1,1-dimethylcyclopropane. These products were obtained from dineopentyl magnesium and dineopentyl oxalate[11]—compounds that are expected to yield the neopentyl free radical upon flash vacuum pyrolysis.

The R--O bond of at least one alkoxide ligand must remain unbroken during ether formation, since it is unlikely that ethers arise by the termolecular combination of two hydrocarbyl radicals with one oxygen atom. Therefore, the formation of diallylcarbinyl ether implies that the homolysis of the R--O bond in **5** (eq 1) occurs in a step that is separate from those involved in ether formation (eq 2).


(2)

A further feature of the pyrolysis that emerges upon examination of the product distribution is that, with the exception of **4**, the ratio of alcohol to ether formed increases markedly on going from primary (**1** and **5**) to secondary (**2**) to tertiary (**3**) alkoxide, i.e., with increasing steric crowding at the α-carbon. This observation is most easily explained by a mechanism encompassing eqs 2 and 3. Both involve nucleophilic attack by an incipient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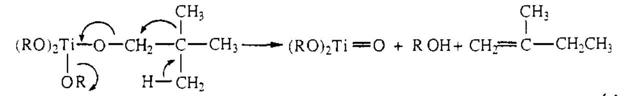
alkoxide ion. As the α-carbon becomes less accessible, attack on the β-hydrogen becomes more prevalent. Steric crowding at the α-carbon also causes the hydrogen atoms of the β-methyl group to approach the oxygens of the neighboring alkoxide groups. Note that the allylcarbinyl derivatives obtained from **5** arise through an additional radical-induced ring-opening step[9] (eq 1). Although the neopentoxide derivative, **4**, is a primary alkoxide, it appears to undergo decomposition mainly by attack on the γ-hydrogen (eq 4). However, this is not surprising since models show that these hydrogens are quite close to the neighboring alkoxide oxygens. The skeletal rearrangement shown in eq 4 was previously


(4)

invoked to explain the formation of 2-methylbutenes by the dehydration of neopentyl alcohol on alumina.[12] Again, the intermediacy of a discrete carbocation is unlikely due to the lack of solvent stabilization in the gas phase.

Significant quantities of carbonyl compounds are formed during the pyrolysis of **1** and **2**. Since alkoxide radicals are not involved (vide supra), these are presumably formed by a β-hydrogen abstraction step (eq 5). Facile β-hydrogen abstraction from metal

$$(RO)_2Ti(OR){-}O{-}CH_2CH_3 \xrightarrow[\text{abst.}]{\beta\text{-H}} O{=}CHCH_3 + (RO)_2Ti(OR){-}H \longrightarrow (RO)_2Ti + ROH \qquad (5)$$

alkoxides has been reported previously.[3b] Note that eq 5 involves a net $2e^-$ reduction of titanium (from +4 to +2). Hence the oxidation level of the metal in the titanium oxide derived from **1** should be lower than that derived from an alkoxide lacking β-hydrogens (e.g., **3**). We are currently examining this possibility. If the conclusion is valid, it opens up the interesting possibility of varying the oxidation level of the metal in oxides by the proper choice of the precursor alkoxide complexes.

In conclusion, our study allows, for the first time, the delineation of the multitude of mechanistic steps involved in the thermal decomposition of metal alkoxides.

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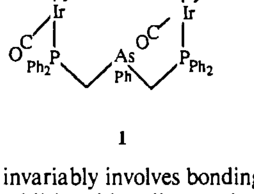
Metal Ions as Ligands: Complexation of Tin(II) Chloride by the Bidentate Ligand $[Ir_2(CO)_2Cl_2\{Ph_2P(CH_2)_4PPh\}_2]$

We have reported that the metallamacrocycle **1**, $Ir_2(CO)_2Cl_2(\mu\text{-dpma})_2$, reacts with a variety of transition-metal ions and main-group ions to form complexes in which metal ions are bound to the center of the cavity.[1] For transition metals, this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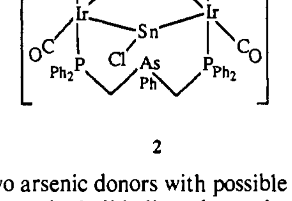
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invariably involves bonding to the two arsenic donors with possible additional bonding to the iridium ions, the halide ligands, or the carbonyl groups. A few main-group ions (Sn^{II}, Pb^{II}, Tl^{I}) bind to **1**, but the structural information suggests that bonding is exclusively through the iridium ions, as shown in **2**.[2,3] Metal-

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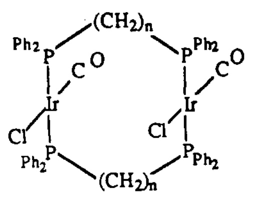
lamacrocycles such as **3**, which lack the arsenic atoms, should also



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be capable of binding these main-group ions, but they should also be more selective in their binding, since they lack the arsine functionality that is necessary for coordination to transition-metal ions. Initial work on the large-ring compounds, **3**, focused on issues of ligand bridges versus chelate ring formation, cyclometalation, dehydrogenation of the aliphatic backbone, and addition of small molecules.[4] Here we describe the preparation of $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ (**3**, *n* = 4, dppb is 1,4-bis(diphenylphosphino)butane) and its ability to complex tin and other metal ions.

Treatment of $Ir(CO)_2Cl(p\text{-toluidine})$ with dppb in toluene at 50–55 °C produced a yellow powder after cooling. Yellow-orange crystals of $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ ($^{31}P\{^1H\}$ NMR singlet, 18.0 ppm in chloroform; IR ν(CO) 1946 cm^{-1} (mineral oil mull)) were isolated by fractional crystallization from dichloromethane/methanol in 30–50% yield. The structure, as determined by X-ray crystallography, is shown in Figure 1.[6] The 14-membered ring is centrosymmetric with the two iridium ions separated by 6.683 (1) Å.

Addition of anhydrous tin(II) chloride to a tetrahydrofuran solution of $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ produces a blue solution, from which crystals of $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$ were obtained by concentration and storage at −5 °C for 5 days. Two views of the structure, as determined by X-ray crystallography, are shown in Figure 2.[7] The adduct consists of the intact metallamacrocycle with the tin atom bonded to it through the two iridium atoms. It has crystallographicaly imposed C_2 symmetry, with the C_2 axis running through the tin atom and bisecting the Cl(2)–Sn–Cl(2′) angle. The tin atom is four-coordinate but considerably distorted from idealized tetrahedral coordination. The Ir–Sn–Ir angle of 138.9 (1)° is considerably wider than 109°, while the Cl(2)–Sn–Cl(2′) angle (90.2 (4)°) is much narrower. The Sn–Cl(2) distance (2.459 (9) Å) is similar to that seen in **2** (2.443 (7) Å)[3] and just slightly shorter than the range (2.47–3.10 Å) of Sn–Cl distances seen in $[SnCl_4]^{2-}$.[8] The Ir–Sn distance (2.751 (1) Å) is very similar to those in **2** (2.741 (2), 2.742 (2) Å)[3] but somewhat longer than the range of Sn–Ir distances (2.57–2.64 Å) seen in complexes containing the Ir–$SnCl_3$ unit.[9]

The metallamacrocycle in the tin chloride adduct has retained its basic structure but has undergone some significant changes. The ClIr(CO) units no longer have the trans geometry seen in the empty macrocycles. Rather, they have a cis arrangement in

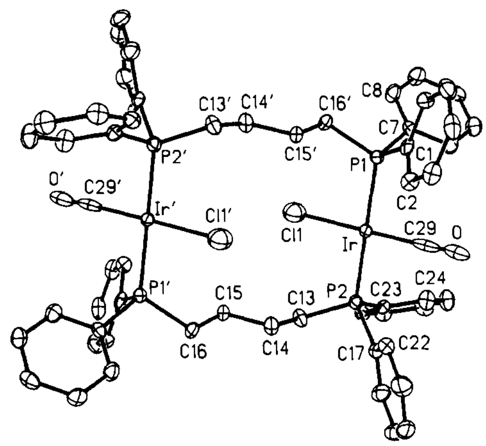

Figure 1. Perspective view of $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ (**4**) with 50% thermal contours for heavy atoms and uniform, arbitrarily sized circles for carbon atoms. Selected distances (Å): Ir–P(1), 2.321 (2); Ir–P(2), 2.322 (2); Ir–Cl(1), 2.350 (3); Ir–C(29), 1.888 (10); Ir···Ir′, 6.683. Angles (deg): P(1)–Ir–P(2), 175.9 (1); Cl(1)–Ir–C(29), 178.2 (3).

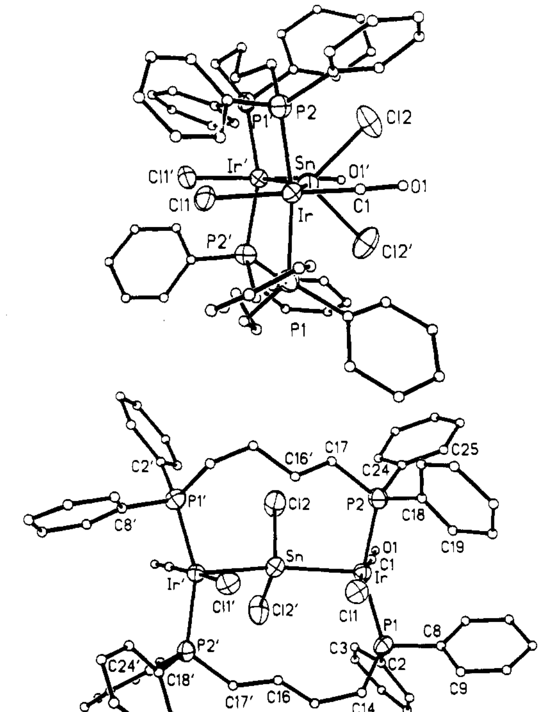

Figure 2. Two views of $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$ showing 50% thermal contours for the heavy atoms and uniform, arbitrarily sized circles for the carbon and oxygen atoms. Selected distances (Å): Ir–P(1), 2.339 (8); Ir–P(2), 2.341 (8); Ir–Cl(1), 2.364 (7); Ir–C(1), 1.84 (3); Ir–Sn, 2.751 (1); Sn–Cl(2), 2.459 (9); Ir···Ir′, 5.151 (1). Angles (deg): P(1)–Ir–P(2), 151.4 (3); Cl(1)–Ir–C(1), 175.3 (9); Ir–Sn–Ir, 138.8 (1); Cl(2)–Sn–Cl(2′), 90.2 (4); Ir–Sn–Cl(2), 99.3 (2); Ir–Sn–Cl(2′), 109.6 (2).

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(5) Sanger in ref 4f reports a singlet at 1.7 ppm for a purported trimer, $Ir_3(CO)_3Cl_3(\mu\text{-dppb})_3$. We have not observed any resonance in the vicinity of 1.7 ppm in our preparations.

(6) Yellow-orange parallelepipeds of $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2{\cdot}2CH_2Cl_2$ crystallize in the triclinic space group $P\bar{1}$ (No. 2) with *a* = 9.333 (2) Å, *b* = 11.611 (2) Å, *c* = 14.451 (3) Å, α = 74.90 (1)°, β = 85.45 (1)°, and γ = 77.8 (1)° at 130 K with *Z* = 1. Refinement of 4418 reflections with $I > 2\sigma(I)$ and 334 parameters yielded *R* = 0.039, R_w = 0.040.

(7) Green plates of $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2{\cdot}2C_4H_8O$ crystallize in the monoclinic space group *C*2/*c* (No. 15) with *a* = 27.406 (15) Å, *b* = 17.026 (6) Å, *c* = 15.410 (9) Å, and β = 91.11 (5)° at 130 K with *Z* = 4. Refinement of 2513 reflections with $I > 2\sigma(I)$ and 211 parameters yielded *R* = 0.081, R_w = 0.085.

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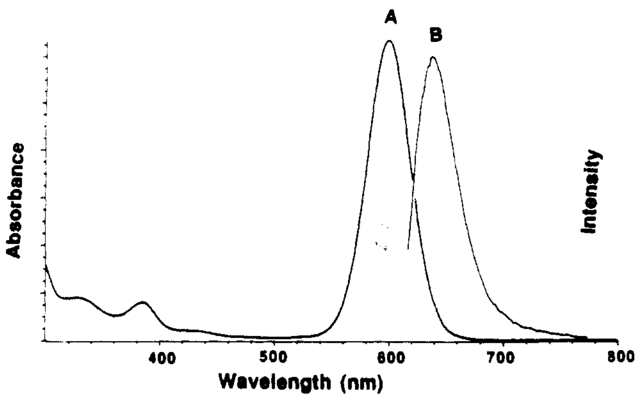

Figure 3. (A) Electronic absorption and (B) uncorrected emission (λ_{exc} 600 nm) spectra of a dichloromethane solution of $[Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2]$.

the adduct. This change may have been accomplished by rotation of the ClIr(CO) unit about its P–Ir–P axis. The 6.683 (1)-Å separation between the two iridium atoms in the open metallamacrocycle appears sufficient to allow for passage of one Ir–Cl unit through the central space. The second change involves a pronounced bending of the P–Ir–P angle. In the adduct this angle is 151.4 (3)°, while it is nearly linear (175.9 (1)°) in the free metallamacrocycle. This bending allows the two iridium atoms to approach the tin atom and results in a net contraction of the Ir···Ir separation by 1.532 Å (to 5.151 (1) Å) in the adduct. This bending appears to have only minor consequences on the Cl–Ir–CO unit, which remains essentially linear.

The adduct retains its structure in dichloromethane or tetrahydrofuran solution. The $^{31}P\{^1H\}$ NMR spectrum consists of a singlet at 9.75 ppm with satellites due to coupling to tin (^2J(Sn,P) = 96.7 Hz). The electronic absorption spectrum of the adduct is shown in Figure 3. An intense feature at 600 nm (ϵ = 45 000 M^{-1} cm^{-1}) is responsible for the blue color. The complex is luminescent with an intense emission, with λ_{max} = 647 nm. The small Stokes shift and the mirror image relation to the absorption spectrum suggest that the emission arises from fluorescence. Solutions of this adduct are very sensitive to air. Exposure to the atmosphere results in bleaching of the blue color. The $^{31}P\{^1H\}$ NMR spectrum indicates that the free metallamacrocycle, $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$, which does not bind dioxygen, is liberated in this process.

$Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$ and $[Ir_2(SnCl)(CO)_2Cl_2(\mu\text{-dpma})_2]^+$ have a number of important differences. The first is a neutral molecule, while the latter is a monocation. The tin is four-coordinate in the former, but three-coordinate and planar in the latter. Nevertheless, the electronic absorption and emission spectra of the two are similar. Thus the added chloride ligand in $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$ serves only to fill a vacant tin orbital and does not perturb the essential chromophore, which involves the filled d_{z^2} orbitals on iridium, the filled s orbital on tin, and the empty p orbitals on both iridium and tin.[3] $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$ is sensitive to oxidation by air, whereas $[Ir_2(SnCl)(CO)_2Cl_2(\mu\text{-dpma})_2]^+$ is not. Treatment of the latter with an excess of 18-crown-6 in dichloromethane results in the removal of the $SnCl^+$ unit, while 18-crown-6 has no effect on solutions of $Ir_2(SnCl_2)(CO)_2Cl_2(\mu\text{-dppb})_2$.

$Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ does not react with either (Me_2SAuCl) or $[AuCl_4]^-$, species which readily add to **1**.[10] It does, however, form pink and orange complexes on treatment with lead(II) acetate or thallium(I) nitrate. Thus, it appears to have the selectivity that we anticipated. Further studies on complexes of the type **3** with varying ring sizes are in progress.

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Supplementary Material Available: Tables of all atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal refinement data for $Ir_2(CO)_2Cl_2(\mu\text{-dppb})_2$ and its tin(II) chloride adduct (13 pages); listings of observed and calculated structure factors (41 pages). Ordering information is given on any current masthead page.

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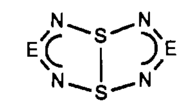
A Novel Coordination Mode for Dithiatetrazocines: Preparation, X-ray Structure, and Fluxional Behavior of $[Pt(PPh_3)(1,5\text{-}Ph_4P_2N_4S_2)]_2$

The coordination chemistry of inorganic sulfur–nitrogen (S–N) ligands has been an area of considerable recent activity.[1,2] The interaction of tetrathiatetrazocine, S_4N_4, with the platinum group metals usually results in fragmentation of the ligand to give metal complexes of S–N anions.[1,2] There are two complexes, $Ir(CO)Cl(S_4N_4)(PPh_3)$[3] and $Pt(S_4N_4)Cl_2(PMe_2Ph)$,[4] which incorporate the tridentate (N,S,S) $S_4N_4^{2-}$ ligand formed by insertion of the metal into an S–N bond. In contrast, we have shown that the integrity of dithiatetrazocines $E_2N_4S_2$ (**1a**, E = Me_2NC; **1b**, E = Ph_2P) is retained in the formation of 1:1 complexes with



1a, E = Me_2NC
b, E = PPh_2

platinum, $Pt(E_2N_4S_2)(PPh_3)_2$ (**2a**, E = Me_2NC; **2b**, E = Ph_2P), in which the metal–ligand bonding is analogous to that found in η^2-alkene–platinum complexes.[5] We report here the preparation and X-ray structural characterization of the binuclear complex $[Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)]_2$ (**3**) in which the ligand **1b** exhibits a novel bonding mode. A variable-temperature ^{31}P NMR spectroscopic study of **3** provides evidence for the first example of a metallotropic rearrangement in coordination complexes of S–N ligands.

The thermal decomposition of **2b** in solution results in the dissociation of triphenylphosphine and the formation of the binuclear complex, **3**.[6] This process is reversible; the addition of 2 molar equivalents of Ph_3P to a solution of **3** in CH_2Cl_2 slowly regenerates **2b**.

$$2Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)_2 \underset{+2PPh_3}{\overset{-2PPh_3}{\rightleftharpoons}} [Pt(1,5\text{-}Ph_4P_2N_4S_2)(PPh_3)]_2 \quad (1)$$

The structure of **3** was determined by X-ray crystallography.[7] The molecular geometry and atomic numbering scheme are shown in Figure 1. The $P_2N_4S_2$ rings in **3** act as chelating (N,S) ligands toward one platinum and form a bridge to the second platinum via the other sulfur atom to give a centrosymmetric dimeric structure. The geometry around platinum is approximately square planar. The sulfur atoms are both three-coordinate and trans to each other, and the Pt–S bond lengths are equal. The coordination to platinum results in significant distortions of the geometry of

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(5) Chivers, T.; Dhathathreyan, K. S.; Ziegler, T. *J. Chem. Soc., Chem. Commun.* **1989**, 86. Preliminary X-ray structural data have established η^2-S,S′ bonding for **2a**, but the structure of **2b** has not been ascertained.
(6) A solution of **2b**[5] (0.25 mmol) in toluene (30 mL) was heated at 105 °C for 6 h under an atmosphere of dry N_2. The bright yellow precipitate of **3** (0.10 mmol, 80%) was isolated by use of a filter needle and identified by X-ray crystallography. ^{31}P NMR data for **3** are given in the text.

