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Trapping of Three-Center Ir–Sn–X Intermediates in the Reaction of Ir^I[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) with Organotin(IV) Halides. X-ray Structure of [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(Br)SnMe$_2$Br

Adolphus A. H. van der Zeijden,[†] Gerard van Koten,*,[†] Jacqueline M. A. Wouters,[†] Willem F. A. Wijsmuller,[†] David M. Grove,[†] Wilberth J. J. Smeets,[‡] and Anthony L. Spek[‡]

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands. Received November 5, 1987
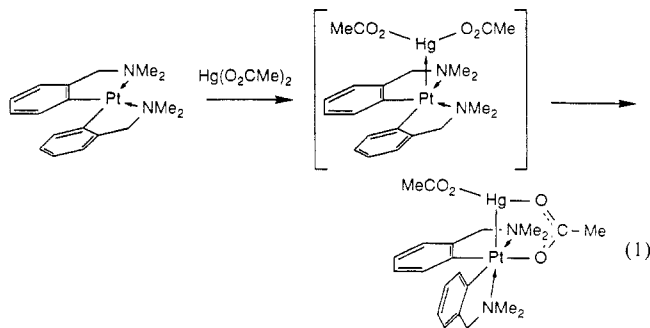
Abstract: The reaction of Ir^I[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) with various organotin(IV) halides SnRR′X$_2$ yields dinuclear adducts [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(X)SnRR′X (X = Cl, R = R′ = Me, Ph; X = R = Cl, R′ = Me; X = Br, R = R′ = Me, Br; X = Br, R = Me, R′ = Ph). No reaction was observed with SnMe$_3$Cl. The X-ray structure of [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(Br)SnMe$_2$Br was determined. Crystals are triclinic, space group P$\bar{1}$, with unit-cell dimensions a = 10.122 (2) Å, b = 14.136 (2) Å, c = 17.310 (2) Å, α = 66.83 (1)°, β = 69.35 (1)°, γ = 73.64 (2)°. The crystal structure was solved with direct methods (Ir, Sn, Br) and subsequent difference Fourier techniques. Anisotropic blocked full-matrix least-squares refinement with 6605 observed reflections and 458 parameters converged at R_F = 0.0337. The molecule contains an Ir–Sn–Br triangle, which appears to be the result of an Sn–Br bond that is side-on coordinated to Ir. As such it can be envisaged as a unique "trapped" three-center intermediate in the concerted oxidative addition of a metal–halide bond to a square-planar metal d^8 complex.

Oxidative addition is a collective term for various means of electron transfer from a metal center to a substrate. Several mechanisms for this process, which is accompanied by quite dramatic changes in the electronic and geometric environment of the metal, have been proposed.[1] In a particular case, the type of mechanism that occurs has been found to be very sensitive to many factors including the nature of the metal complex, the substrate, and the solvent.[1] With d^8 metal complexes the addition mechanisms of dihydrogen, silanes, hydrogen halides, and alkyl halides have been much studied, but those of halogens and metal halides less so. It has been shown that, in general, concerted cis addition takes place for dihydrogen and silanes, while for the other cases several mechanisms, all involving electrophilic attack of the substrate on the nucleophilic metal center, have been proposed.[1]

Both cis and trans oxidative additions of metal (pseudo)halides (especially d^{10} Hg^{II}, Tl^{III}, and Sn^{IV} salts) to d^8 metal complexes have long been known.[2,3] For example, the complex [2-(Me$_2$NCH$_2$)C$_6$H$_4$]$_2$Pt(μ-O$_2$CMe)Hg(O$_2$CMe) (eq 1), isolated by

Van der Ploeg et al., can be considered as a "trapped" intermediate in the concerted cis addition of a mercury–acetato bond to *cis*-Pt^{II}[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$.[4] The first step in this reaction was thought to be the formation of an intermediate adduct with a donative Pt to Hg bond (eq 1). In the case of *trans*-Pt^{II}[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$, an adduct of this type was indeed observed, but further reaction led to elimination of Hg^0 and formation of Pt^{IV}(O$_2$CMe)$_2$[C$_6$H$_4$(CH$_2$NMe$_2$)-2]$_2$.[4]

The fact that such platinum–mercury species can be detected, and sometimes even be isolated, can be attributed to the presence of the chelating ortho-CH$_2$NMe$_2$-substituted aryl ligands which provide some protection against low-energy decomposition pathways and further reactions. The use of this type of ligand has been recently extended to rhodium and iridium, and d^8 Rh^I and Ir^I derivatives, especially, were found to be very reactive toward a variety of electrophiles. Oxidative addition, not accompanied by M–C bond breakage, occurs with Rh^I[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) (COD = 1,5-cyclooctadiene) and MeI, yielding Rh^{III}(Me)I[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6],[5] and with Ir^I[C$_6$H$_4$-(CH$_2$NMe$_2$)-2](COD) and H$_2$, yielding Ir^{III}H$_2$[C$_6$H$_4$-(CH$_2$NMe$_2$)-2](COD) (stable below 0 °C).[6] The complex Rh^I[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) also reacts with a variety of metal salts, resulting in either M–C bond cleavage (transmetalation) with Hg^{II} and Sn^{IV} halides or oxidation of the metal center without M–C bond breakage with Ag^I salts.[7] The mechanisms operating for the former transmetalation reactions were thought not to be based on the rhodium center but rather to proceed through electrophilic attack of the metal salt on the Rh–C(aryl) bond or on the C(aryl) atom itself.[7] In this paper we report the reaction of related Ir^I[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) with organotin(IV) halides that affords unique iridium–tin adducts

* To whom correspondence should be addressed at the Laboratory of Organic Chemistry, University of Utrecht, Dept. of Metal Mediated Synthesis, Padualaan 8, 3584 CH Utrecht, The Netherlands.
† University of Amsterdam.
‡ University of Utrecht.

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Trapping of Three-Center Ir–Sn–X Intermediates

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which can be regarded as "trapped" intermediates in the concerted cis oxidative addition of a tin–halide bond to an iridium(I) center.

Experimental Section

General Methods. All manipulations were performed at room temperature under an atmosphere of nitrogen with use of Schlenk techniques. Ir[C₆H₃(CH₂NMe₂)-2-R-6](COD) (R = H, Me, CH₂NMe₂) were prepared according to ref 8. Solvents were carefully dried and distilled prior to use. ¹H NMR spectra were recorded on a Bruker WM250 spectrometer. Elemental analyses were carried out by the Analytical Department of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. Molecular weights were determined in CH₂Cl₂ by using a HP 320B vapor pressure osmometer (estimated error: ±10%, c = 0.01 mol/L).

Synthesis of [2-(Me₂NCH₂)C₆H₄](COD)Ir(X)SnRR′X (1–6). To a stirred solution of Ir[C₆H₄(CH₂NMe₂)-2](COD) (ca. 50 mg) in benzene or toluene (5 mL) was added an equimolar quantity of SnRR′X₂. Within a few seconds the red solution became pale yellow and within 5–60 min a yellow solid was deposited (with SnBr₄ a red solid precipitated instantaneously). This solid was filtered off, washed with pentane (5 mL), and dried in vacuo: yield 60–90%. The compounds are moderately air-stable. Ir[C₆H₄(CH₂NMe₂)-2](COD) did not react with SnMe₃Cl under these conditions.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Cl)SnMe₂Cl (1): mol wt calcd 654, found 607.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br (2): mol wt calcd 743, found 701. Anal. Calcd for C₁₉H₃₀Br₂IrNSn: C, 30.71; H, 4.07; Br, 21.50; N, 1.89. Found: C, 30.56; H, 4.23; Br, 21.40; N, 2.05. Crystals of the complex, suitable for a single-crystal X-ray diffraction study, were formed from a freshly prepared 1:1 mixture of Ir[C₆H₄(CH₂NMe₂)-2](COD) and SnMe₂Br₂ in benzene upon standing for a few hours.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Cl)SnPh₂Cl (3): mol wt calcd 778, found 787. Anal. Calcd for C₂₉H₃₄Cl₂IrNSn: C, 44.75; H, 4.40; Cl, 9.11; N, 1.80. Found: C, 44.65; H, 4.59; Cl, 8.77; N, 1.74.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMePhBr (4): Anal. Calcd for C₂₄H₃₂Br₂IrNSn: C, 35.80; H, 4.01; Br, 19.85; N, 1.74. Found: C, 36.94; H, 4.34; Br, 20.15; N, 1.58.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Cl)SnMeCl₂ (5): Anal. Calcd for C₁₈H₂₇Cl₃IrNSn: C, 32.04; H, 4.03; Cl, 15.76; N, 2.08. Found: C, 32.57; H, 4.38; Cl, 15.28; N, 1.98.

[2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnBr₃ (6): Anal. Calcd for C₁₇H₂₄Br₄IrNSn: C, 23.39; H, 2.77; Br, 36.61; N, 1.60. Found: C, 23.39; H, 3.21; Br, 36.06; N, 1.55.

Decomposition of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br (2). A freshly prepared solution of Ir[C₆H₄(CH₂NMe₂)-2](COD) (ca. 100 mg) and an equimolar amount of SnMe₂Br₂ in benzene (3 mL) was stirred for 3 days. The off-white precipitate which was formed was filtered off; it probably contained polymeric organotin compounds. The orange filtrate was found to contain a 1:2 mixture of [IrBr(COD)]₂ and C₆H₅CH₂NMe₂ (¹H NMR); the resonances of the 1:1 iridium–tin adduct **2** had disappeared. To this orange filtrate was added 1 N hydrochloric acid (5 mL), and after stirring for a few minutes, the two layers were separated. The benzene layer afforded, after evaporation of the solvent, quantitatively [IrBr(COD)]₂ (identified by ¹H NMR and FD mass spectroscopy). The water layer afforded the white ammonium salt [C₆H₅CH₂N(H)Me₂]Cl in quantitative yield.

The behavior of the other iridium–tin complexes **1** and **3–6** in either C₆D₆ or CD₂Cl₂ was monitored by ¹H NMR. The tin-methyl complexes **1**, **4**, and **5** showed at about the same rate a similar product formation as found for **2**. No decomposition was observed either for **3** or for **6**. The latter complex was also recovered unchanged after stirring for 3 weeks as a suspension in pyridine.

Reaction of Ir[C₆H₃(CH₂NMe₂)-2-R-6](COD) (R = Me, CH₂NMe₂) with SnMe₂Br₂. This reaction was conducted as described above for the decomposition of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br. An instant reaction took place, affording an insoluble white solid (probably containing organotin polymers). The benzene filtrate yielded [IrBr(COD)]₂ quantitatively after workup. When R = Me, the acidic water layer afforded 100% [1-(Me₂(H)NCH₂)-3-Me-C₆H₄]Cl. When R = CH₂NMe₂ a mixture of [1,3-(Me₂(H)NCH₂)₂C₆H₄]Cl₂ (65%) and the tin salt {SnMe₂[C₆H₃(CH₂NMe₂)₂-2,6]}Cl (35%) was obtained (both identified by ¹H NMR,[9] product distribution by integration).

Structure Determination and Refinement of [2-(Me₂NCH₂)C₆H₄]-(COD)Ir(Br)SnMe₂Br (2). A yellow plate shaped crystal was mounted on a glass fiber and transferred to an ENRAF-Nonius CAD-4F diffractometer for data collection. Crystal data and details of the structure

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Table I. Crystal Data and Details of the Structure Analysis of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br

a. Crystal Data (294 K)	
formula	C₁₉H₃₀NBr₂IrSn
mol wt	743.17
cryst system	triclinic
space group	P1̄ (no. 2)
a, b, c (Å)	10.122 (2), 14.136 (2), 17.310 (2)
α, β, γ (deg)	66.83 (1), 69.35 (1), 73.64 (2)
V (Å³)	2101.1(8)
Z	4
D_calcd (g cm⁻³)	2.349
F(000)	1392
μ(Mo Kα) (cm⁻¹)	112.7
cryst size (mm)	0.43 × 0.28 × 0.13

b. Data Collection (294 K)	
Θ_min, Θ_max (deg)	1.9, 27.5
radiation	Zr-filtered Mo Kα, 0.71073 Å
ω/2Θ scan (deg)	0.70 + 0.35 tan Θ
horzntl and vert aperture (mm)	4.0, 4.0
distance cryst to detector (mm)	173
ref reflcns	113, -111, 111
total data	8742
total unique data	8291
obsd data (I > 2σ(I))	6605

c. Refinement	
no. of refined params	458
weighting scheme	w = 1/σ²(F)
final R, R_w, S	0.0337, 0.0364, 1.35
(Δ/σ)_av in final cycle	0.009

determination are given in Table I. Unit cell parameters were determined from a least-squares treatment of the setting angles of 22 reflections in the range 11.4 < θ < 14.2°. The triclinic unit cell was checked for the presence of higher lattice symmetry.[10h] Data were collected for one hemisphere (-13 ≤ h ≤ 0, -13 ≤ k ≤ 13, -18 ≤ l ≤ 18) and corrected for Lp, absorption (Gaussian integration: grid 10 × 10 × 10; maximum and minimum correction: 14.256 and 3.938), and for a linear decay of 3.3% during 187 h of X-ray exposure. Standard deviations based on counting statistics were increased according to an analysis of the excess variance of three reference reflections: σ²(I) = σ²_cs(I) + (0.054I)².[10a] Space group P1̄ was discriminated from P1 during the structure determination process. The equivalent reflections (0k1 and 0k̄1̄) were merged with a consistency index (on I) of 5.54%. The Ir, Sn, and Br atoms were found with direct methods (SHELXS86);[10b] other non-H atoms were located from subsequent difference Fourier maps. Refinement was carried out by blocked full-matrix least-squares techniques (on F) with anisotropic thermal parameters for all non-H atoms. Hydrogen atoms were introduced on calculated positions [d(C-H) = 0.98 Å] and included in the refinement riding on their carrier atom with one common isotropic thermal parameter. Weights were introduced in the final refinement cycles; convergence was reached at R_F = 0.0337. Final positional parameters are listed in Table II. A final difference Fourier synthesis reveals residual density (interpreted as absorption artefact) of 2.92 eÅ⁻³ at 1.05 Å from Ir(1) (molecule 2); all other features are between 1.34 and -1.46 eÅ⁻³. Neutral atom scattering factors were taken from ref 10c and corrected for anomalous dispersion.[10d] Data collection was done with a modified CAD-4F software package.[10e] All calculations were performed with SHELX76[10f] and the EUCLID package[10g] (geometrical calculations and illustrations) on the CDC Cyber-855 of the University of Utrecht.

Results

Synthesis of [2-(Me₂NCH₂)C₆H₄](COD)Ir(X)SnRR′X (1–6). The reaction of the square-planar iridium(I) complex Ir[C₆H₄-

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Table II. Positional and Equivalent Isotropic Thermal Parameters of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br

atom	x	y	z	U (eq),^{a} Å^2
		Molecule 1		
Ir(1)	0.65914 (3)	0.22601 (2)	0.51023 (2)	0.0246 (1)
Sn(1)	0.39949 (5)	0.22127 (4)	0.61738 (3)	0.0304 (2)
Br(1)	0.58781 (8)	0.36399 (6)	0.58707 (5)	0.0389 (3)
Br(2)	0.27533 (9)	0.06958 (7)	0.64128 (6)	0.0517 (3)
N(1)	0.8944 (6)	0.2318 (5)	0.5019 (4)	0.035 (2)
C(1)	0.7072 (7)	0.0970 (5)	0.6132 (4)	0.028 (2)
C(2)	0.8191 (7)	0.0992 (6)	0.6414 (5)	0.034 (2)
C(3)	0.8655 (8)	0.0154 (6)	0.7076 (5)	0.044 (3)
C(4)	0.8062 (9)	−0.0720 (6)	0.7455 (5)	0.050 (3)
C(5)	0.6955 (8)	−0.0801 (6)	0.7188 (5)	0.039 (2)
C(6)	0.6486 (7)	0.0047 (5)	0.6537 (4)	0.032 (2)
C(7)	0.8905 (8)	0.1918 (6)	0.5959 (5)	0.040 (3)
C(8)	1.0060 (8)	0.1596 (7)	0.4622 (6)	0.050 (3)
C(9)	0.9417 (9)	0.3346 (6)	0.4623 (6)	0.048 (3)
C(10)	0.3784 (9)	0.1829 (7)	0.7531 (5)	0.049 (3)
C(11)	0.2316 (8)	0.3472 (6)	0.5774 (5)	0.046 (3)
C(12)	0.792 (1)	0.3155 (6)	0.3106 (5)	0.052 (3)
C(13)	0.7939 (9)	0.1988 (6)	0.3295 (5)	0.046 (3)
C(14)	0.7369 (8)	0.1362 (6)	0.4242 (5)	0.039 (3)
C(15)	0.5899 (8)	0.1308 (5)	0.4639 (5)	0.035 (3)
C(16)	0.4769 (9)	0.1878 (6)	0.4149 (5)	0.046 (3)
C(17)	0.480 (1)	0.3042 (6)	0.3691 (5)	0.050 (3)
C(18)	0.5473 (8)	0.3507 (6)	0.4095 (5)	0.040 (2)
C(19)	0.6888 (9)	0.3572 (6)	0.3813 (4)	0.041 (3)
		Molecule 2		
Ir(1)	0.29323 (3)	0.71655 (2)	0.08009 (2)	0.0282 (1)
Sn(1)	0.13984 (5)	0.57938 (4)	0.20741 (3)	0.0313 (2)
Br(1)	0.07447 (9)	0.80492 (6)	0.17641 (5)	0.0441 (3)
Br(2)	0.2187 (1)	0.38544 (6)	0.20837 (6)	0.0490 (3)
N(1)	0.2709 (7)	0.8791 (5)	−0.0288 (4)	0.046 (3)
C(1)	0.1817 (8)	0.6962 (6)	0.0095 (4)	0.033 (2)
C(2)	0.1119 (8)	0.7899 (6)	−0.0400 (5)	0.040 (3)
C(3)	0.036 (1)	0.7885 (7)	−0.0942 (6)	0.058 (3)
C(4)	0.0267 (9)	0.6955 (8)	−0.0981 (5)	0.057 (4)
C(5)	0.0975 (8)	0.6039 (7)	−0.0526 (5)	0.047 (3)
C(6)	0.1741 (8)	0.6048 (6)	−0.0005 (4)	0.035 (3)
C(7)	0.127 (1)	0.8895 (6)	−0.0377 (6)	0.052 (3)
C(8)	0.375 (1)	0.8814 (7)	−0.1161 (5)	0.062 (3)
C(9)	0.275 (1)	0.9731 (7)	−0.0121 (6)	0.062 (4)
C(10)	−0.0712 (8)	0.5886 (7)	0.2013 (6)	0.049 (3)
C(11)	0.1549 (8)	0.5453 (6)	0.3369 (4)	0.037 (2)
C(12)	0.579 (1)	0.7884 (8)	0.0404 (6)	0.063 (4)
C(13)	0.6194 (9)	0.7070 (7)	−0.0064 (5)	0.052 (3)
C(14)	0.4936 (8)	0.6608 (6)	0.0019 (5)	0.040 (3)
C(15)	0.4455 (7)	0.5748 (6)	0.0732 (5)	0.035 (2)
C(16)	0.5105 (8)	0.5213 (6)	0.1488 (5)	0.044 (3)
C(17)	0.5233 (8)	0.5933 (7)	0.1905 (6)	0.051 (3)
C(18)	0.4145 (8)	0.6916 (7)	0.1801 (5)	0.043 (3)
C(19)	0.4404 (8)	0.7837 (7)	0.1092 (5)	0.044 (3)

$^a U$ (eq) $= \frac{1}{3}\sum_{ij}U_{ij}a_i^*a_j^*a_i a_j$.

(CH₂NMe₂)-2](COD)^8 with an equimolar amount of SnRR′X₂ in either benzene, toluene, or CH₂Cl₂ results within 5–60 min in the formation of a yellow precipitate (red for SnBr₄). These solid products were identified, by a combination of elemental analyses, osmometric measurements in CH₂Cl₂, and ¹H NMR, as being monomeric 1:1 adducts of the two starting compounds (eq 2).

Ir[C₆H₄(CH₂NMe₂)-2](COD) + SnRR′X₂ →
                    [2-(Me₂NCH₂)C₆H₄](COD)IrSnRR′X₂ (2)
                                    1–6
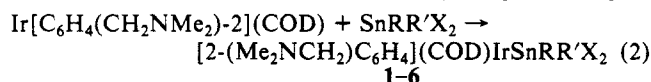
X =, R =, R′ =:   (1) Cl, Me, Me;
(2) Br, Me, Me;   (3) Cl, Ph, Ph;   (4) Br, Me, Ph;
        (5) Cl, Me, Cl;   (6) Br, Br, Br;

The presence of at least two halide atoms on tin appears to be a prerequisite for this adduct formation, since no reaction was observed with this iridium complex and the triorganotin compound SnMe₃Cl. It was also observed that the more halide atoms there were present, the faster adduct formation proceeded. The moderately air-stable adducts are slightly soluble in CH₂Cl₂ and benzene; as the number of tin-bonded halide atoms present increases, so the solubility of the complex decreases.

¹H NMR Spectroscopic Measurements. The ¹H NMR spectral data of the iridium–tin complexes 1–6 measured in CD₂Cl₂ at room temperature are listed in Table III. The resonance patterns of the [C₆H₄(CH₂NMe₂)-2] and COD ligands indicate a lack of molecular symmetry, and in this respect these adducts resemble the iridium(III) dihydride IrH₂[C₆H₄(CH₂NMe₂)-2](COD).^{6} From the appearance of the two benzylic protons as two well-separated AX doublets and of the two NMe₂ methyls as two singlet resonances, it is concluded that the respective C and N centers are diastereotopic. The chirality of the tertiary amine group indicates that the N-atom is coordinated to iridium. The four olefinic protons of COD appear as four separate (sometimes overlapping) resonances between 3.4 and 5.4 ppm.

In the SnMe₂X₂ adducts 1 and 2 there are two singlet resonances between 0.3 and 1.1 ppm, having ^2J(Sn–H) couplings that are characteristic for tin-bonded methyl groups.^{11} The fact that the prochiral SnMe₂ entity affords two separate methyl resonances indicates that the tin center is in some way bonded to the Ir-[C₆H₄(CH₂NMe₂)-2](COD) system, most probably to the iridium center. Consequently, in those adducts where the R and R′ groups of SnRR′X₂ are not the same, as in 4 (SnMePhBr₂) and 5 (SnMeCl₃), one can reason on symmetry grounds that two isomers should be possible. For complex 4, these are indeed observed (designated 4a and 4b in Table III; 4a:4b = 2:1), but for 5 only one of the isomers appears to be present. These different and unequal isomer distributions in 4 and 5 point to significant steric and/or electronic differences in the surroundings of the R and R′ sites in these complexes.

With respect to the parent tin compounds, the resonances of the SnMe groups in the adducts 1, 2, 4a/b, and 5 show upfield chemical shifts that consistently fall into two narrowly defined ranges (see Table III). These ranges of +0.83 (±0.08) (Δ), and +0.27 (±0.02) (Δ′) ppm have associated ^2J(Sn–H) couplings of ca. 63 and 49 Hz, respectively (separate ^{117}Sn and ^{119}Sn couplings were not observed at 250 MHz). These data relate clearly to the two different sites of the R and R′ groups in these adducts. On this basis it can be deduced that the single SnMe group in both 4a and 5 probably resides in the same relative position. It should be noted that although the magnitudes of ^2J(Sn–H) couplings are usually very characteristic for the coordination around tin in its normal mononuclear complexes, the proximity of another metal (Ir) may significantly influence them.^{11}

The ¹H NMR data are consistent with the presence of a direct Ir–Sn interaction in all adducts, but they are insufficient in themselves to allow an unambiguous structural deduction. Therefore an X-ray crystallographic analysis of a representative adduct, [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Br (2), was undertaken.

Solid-State Structure of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)-SnMe₂Br (2). The crystal structure of 2 consists of four discrete molecules in a triclinic unit cell. The asymmetric unit contains two crystallographically independent molecules (numbered 1 and 2). Selected bond distances and angles are listed in Tables IV and V. The differences in the geometrical data of the two molecules are minor, and therefore only the structure of molecule 1 will be described. The structure of molecule 1 and the adopted numbering scheme is shown in Figure 1.

Iridium Coordination Sphere. The coordination sphere of iridium is supplied by two double bonds of COD, the *C,N*-bonded aryl ligand and by both a bromide and tin atom of a SnMe₂Br₂ unit. The midpoint of the double bond C(18)=C(19) [m(2)] and C(1) of the aryl moiety form an almost linear axial arrangement with the iridium center [C(1)–Ir(1)–m(2) = 175.4 (3)°]. Close to a meridional plane that is perpendicular to this axis and which passes through Ir(1) lies the midpoint of the other double bond C(14)=C(15) [m(1)], N(1) of the aryl ligand, and Sn(1) and

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Table III. ¹H NMR Data of [2-(Me₂NCH₂)C₆H₄](COD)Ir(X)SnRR'Xᵃ

	X	R	R'	[2-(Me₂NCH₂)C₆H₄] aryl[b]	CH₂[c]	NMe	COD =CH[d]	SnRR' R[e]	R'[e]	Δ[f]	Δ'[f]
1	Cl	Me	Me	6.94 (m) 7.12 (d) 7.70 (d)	3.18 (d) 4.91 (d)	2.58 3.05	3.49 4.27 (2 H) 4.83	0.55 (60)	1.11 (49)	0.85	0.29
2	Br	Me	Me	6.93 (m) 7.12 (d) 7.65 (d)	3.08 (d) 4.82 (d)	2.70 2.96	3.38 4.21 (2 H) 4.75	0.28 (60)	0.92 (49)	0.91	0.27
3	Cl	Ph	Ph	g 7.22 (d) 7.88 (d)	3.18 (d) 5.02 (d)	2.76 2.98	3.54 4.26 4.58 4.66	6.7–8.1 (m)			
4a	Br	Me	Ph	6.97 (m) 7.16 (d) 7.93 (d)	3.18 (d) 4.96 (d)	2.70 3.02	3.57 4.22 4.40 4.50	0.73 (63)	h	0.76	
4b	Br	Ph	Me	g	g	2.74 3.07	g	g	1.24ᵍ		0.25
5	Cl	Me	Cl	6.99 (m) 7.19 (d) 7.61 (d)	3.09 (d) 4.93 (d)	2.76 3.00	3.46 4.44 4.56 5.44	0.86 (67)		0.83	
6	Br	Br	Br	7.03 (m) 7.22 (d) 7.60 (d)	3.18 (d) 5.16 (d)	2.74 3.08	3.73 4.19 4.82 (2 H)				

ᵃ Measured in CD_2Cl_2 at 250 MHz; chemical shifts relative to external TMS. ᵇ $^3J(H-H) = 7$ Hz. ᶜ AX doublets with $^2J(H-H) = 13$ Hz. ᵈ Broad resonances. ᵉ $^2J(Sn-H)$ between parentheses; ^{117}Sn and ^{119}Sn couplings were not resolved. ᶠ Δ = difference of the proton chemical shifts of SnMe, between that in the pure tin(IV) compound and the iridium–tin complex. ᵍ Resonances obscured. ʰ 7.34 (m, para/meta), 8.01 (m, ortho).
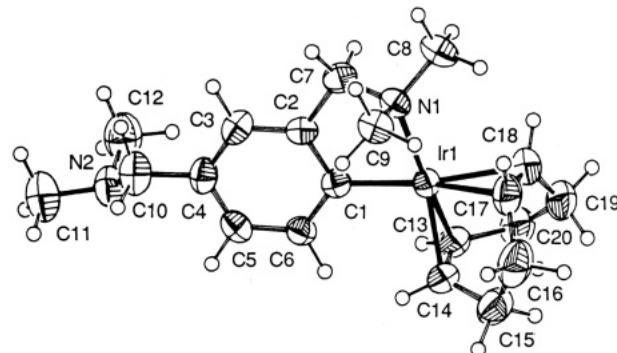
Table IV. Selected Bond Distances (Å) of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)SnMe₂Brᵃ

	molecule 1	molecule 2		molecule 1	molecule 2
			(a) Around Iridium		
Ir(1)–Sn(1)	2.6297 (8)	2.6358 (8)	Ir(1)–C(18)	2.297 (8)	2.324 (9)
Ir(1)–Br(1)	2.582 (1)	2.592 (1)	Ir(1)–C(19)	2.257 (7)	2.253 (9)
Ir(1)–N(1)	2.357 (7)	2.342 (7)	Ir(1)–m(1)	2.033 (8)	2.038 (9)
Ir(1)–C(1)	2.072 (7)	2.069 (8)	Ir(1)–m(2)	2.174 (8)	2.180 (9)
Ir(1)–C(14)	2.132 (8)	2.138 (8)	Ir(1)–m(3)	2.1538 (9)	2.1638 (9)
Ir(1)–C(15)	2.173 (8)	2.173 (8)			
			(b) Around Tin		
Sn(1)–Br(1)	2.934 (1)	2.934 (1)	Sn(1)–C(10)	2.137 (8)	2.141 (9)
Sn(1)–Br(2)	2.608 (1)	2.626 (1)	Sn(1)–C(11)	2.166 (9)	2.152 (7)
			(c) Within Aryl Ligand		
C(2)–C(7)	1.48 (1)	1.48 (1)	⟨C(sp²)–C(sp)⟩	1.39 (2)	1.39 (2)
⟨N(1)–C⟩	1.48 (1)	1.487 (9)			
			(d) Within COD Ligand		
C(14)–C(15)	1.41 (1)	1.40 (1)	⟨C(sp²)–C(sp³)⟩	1.52 (1)	1.51 (2)
C(18)–C(19)	1.36 (1)	1.41 (1)	⟨C(sp³)–C(sp³)⟩	1.54 (1)	1.53 (1)

ᵃ m(1) is the midpoint of C(14)–C(15), m(2) is the midpoint of C(18)–C(19), and m(3) is the midpoint of Sn(1)–Br(1).
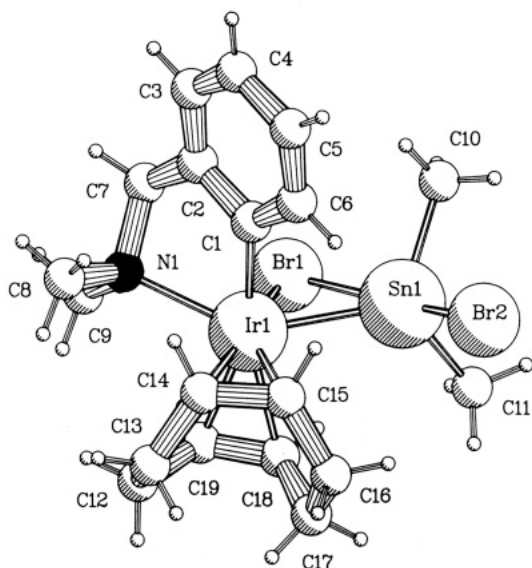
Figure 1. X-ray structure of [2-(Me₂NCH₂)C₆H₄](COD)Ir(Br)-SnMe₂Br (2) (molecule 1).

Figure 2. X-ray structure of Ir[C₆H₃(CH₂NMe₂)₂-2,4](COD) (7).[8]

Br(1) of the SnMe₂Br₂ unit. The resulting octahedral geometry is far from regular, because the four meridional interligand angles deviate significantly from 90°, i.e., m(1)–Ir(1)–Sn(1) = 101.0 (2), Sn(1)–Ir(1)–Br(1) = 68.51 (3), Br(1)–Ir(1)–N(1) = 84.1 (2), and N(1)–Ir(1)–m(1) = 110.0 (3)°. However, if the Sn-(1)–Br(1) bond, with m(3) as its midpoint, is considered as one side-on coordinated ligand, the iridium center then has a fairly regular five-coordinate trigonal bipyramidal geometry. The angles in the trigonal plane, defined by Ir(1), N(1), m(1) and m(3), are then as follows: m(1)–Ir(1)–m(3) = 134.0 (2), m(3)–Ir(1)–N(1) = 114.8 (2), and N(1)–Ir(1)–m(1) = 110.0 (3)°. The Sn(1)–Br(1) bond is twisted 24° around Ir(1)–m(3) out of the equatorial

plane. The nontrivial implications of this geometry and the resulting bonding description are dealt with in the Discussion.

The distance from iridium to the midpoint of the axial double bond of COD [m(2)] is longer than to that of the equatorial one [m(1)] [2.174 (8) versus 2.033 (8) Å], in accord with earlier observations on five-coordinated iridium(I) diene species.[13] The former bond length is one of the longest iridium(I)–olefin bonds encountered so far. The geometry of the C,N-bonded aryl ligand in 2 resembles that in square-planar Ir[C₆H₃(CH₂NMe₂)₂-2,4](COD) (7), see X-ray structure in Figure 2.[8] The Ir–C(aryl) distance of 2.072 (7) Å is close to that in 7 [2.070 (8) Å], but the Ir–N distance of 2.357 (7) Å is significantly longer than in 7 [2.164 (3) Å]. The geometrical constraints of this chelating

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Table V. Selected Bond Angles (deg) of
[2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(Br)SnMe$_2$Br[a]

	molecule 1	molecule 2
(a) Around Iridium		
Sn(1)-Ir(1)-Br(1)	68.51 (3)	68.26 (3)
Sn(1)-Ir(1)-N(1)	142.0 (2)	141.8 (2)
Sn(1)-Ir(1)-C(1)	81.8 (2)	81.2 (2)
Sn(1)-Ir(1)-m(1)	101.0 (2)	99.7 (2)
Sn(1)-Ir(1)-m(2)	101.1 (2)	102.5 (2)
Br(1)-Ir(1)-N(1)	84.1 (2)	84.0 (2)
Br(1)-Ir(1)-C(1)	97.6 (2)	96.6 (2)
Br(1)-Ir(1)-m(1)	164.8 (3)	163.9 (2)
Br(1)-Ir(1)-m(2)	86.7 (2)	88.1 (2)
N(1)-Ir(1)-C(1)	76.1 (3)	76.4 (3)
N(1)-Ir(1)-m(1)	110.0 (3)	111.4 (3)
N(1)-Ir(1)-m(2)	103.1 (3)	102.1 (3)
C(1)-Ir(1)-m(1)	91.4 (3)	91.9 (3)
C(1)-Ir(1)-m(2)	175.4 (3)	174.9 (3)
m(1)-Ir(1)-m(2)	84.7 (3)	84.1 (3)
N(1)-Ir(1)-m(3)	114.8 (2)	114.6 (2)
C(1)-Ir(1)-m(3)	89.6 (2)	88.6 (2)
m(1)-Ir(1)-m(3)	134.0 (2)	132.7 (2)
m(2)-Ir(1)-m(3)	94.8 (2)	96.4 (2)
Ir(1)-Br(1)-Sn(1)	56.52 (3)	56.57 (3)
(b) Around Tin		
Ir(1)-Sn(1)-Br(1)	54.97 (3)	55.17 (3)
Ir(1)-Sn(1)-Br(2)	116.35 (4)	116.59 (4)
Ir(1)-Sn(1)-C(10)	117.4 (3)	116.7 (3)
Ir(1)-Sn(1)-C(11)	117.4 (2)	116.5 (2)
Br(1)-Sn(1)-Br(2)	169.47 (4)	170.87 (4)
Br(1)-Sn(1)-C(10)	85.9 (3)	88.1 (3)
Br(1)-Sn(1)-C(11)	93.3 (2)	92.3 (2)
Br(2)-Sn(1)-C(10)	94.3 (3)	93.2 (3)
Br(2)-Sn(1)-C(11)	96.5 (2)	95.4 (2)
C(10)-Sn(1)-C(11)	110.7 (3)	114.2 (3)
(c) Within Aryl Ligand		
⟨C-N(1)-C⟩	107.0 (9)	107.2 (4)
Ir(1)-N(1)-C(7)	101.5 (5)	102.3 (5)
Ir(1)-N(1)-C(8)	114.8 (5)	113.4 (5)
Ir(1)-N(1)-C(9)	118.0 (5)	118.7 (5)
Ir(1)-C(1)-C(2)	115.7 (5)	114.4 (6)
Ir(1)-C(1)-C(6)	128.1 (5)	129.3 (6)
C(2)-C(1)-C(6)	115.9 (6)	116.2 (7)
N(1)-C(7)-C(2)	109.7 (7)	108.8 (7)
(d) Within COD Ligand		
⟨C(sp^2)-C(sp^2)-C(sp^3)⟩	122.5 (4)	122.5 (9)
⟨C(sp^2)-C(sp^3)-C(sp^3)⟩	114.4 (9)	114.5 (5)

[a] m(1) is the midpoint of C(14)-C(15), m(2) is the midpoint of C-(18)-C(19), and m(3) is the midpoint of Sn(1)-Br(1).

organic ligand impose an acute N(1)-Ir(1)-C(1) angle of 76.1 (3)° [compare 80.4 (2) in **7**].

For **2** the distortion (D) from a trigonal bipyramid toward a square pyramid along the Berry pseudorotation coordinate is only 23%,[12] and in this respect it is surprisingly closer to a perfect trigonal bipyramidal geometry than other five-coordinate iridium(I) diene structures, such as IrMe(COD)(PMe$_2$Ph)$_2$ (D = 40%),[13a] IrMe(COD)[Ph$_2$P(CH$_2$)$_2$PPh$_2$] (D = 62%),[13b] IrMe-(COD)[Ph$_2$P(CH$_2$)$_3$PPh$_2$] (D = 53%),[13c] IrSnCl$_3$(COD)$_2$ (D = 48%),[13d] IrSnCl$_3$(NBD)(PMe$_2$Ph)$_2$ (D = 78%),[13e] and IrCl-(COD)((+)-diop) (D = 41%).[13f] As for **2** they all have an axi-ally/equatorially coordinated diene ligand with, as anticipated, the most electronegative ligand in the other axial position.
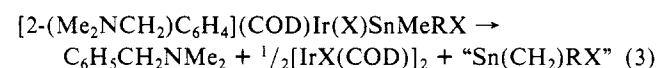
The formation of **2** from square-planar Ir[C$_6$H$_4$-(CH$_2$NMe$_2$)-2](COD), whose structure will be similar to that of Ir[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,4](COD) (**7**, Figure 2),[8] can be easily visualized. As the tin(IV) compound approaches for coordination to iridium, the straight C(aryl)-(Ir)-m(olefin) axis apparently remains intact, while the other double bond and the N-atom rotate toward each other about this axis, by ca. 65°, to form **2**.

Tin Coordination Sphere. As with the iridium atom the best practicable, though not perfect, description of the tin moiety is

based on a trigonal bipyramidal geometry. Around the tin atom, the two bromine atoms occupy the axial positions [Br(1)-Sn-(1)-Br(2) = 169.47 (4)°], and the two carbon atoms of the methyl groups reside in the equatorial plane [C(10)-Ir(1)-C(11) = 110.7 (3)°]. The third position in this plane seems to be vacant; the Ir(1) atom lies closest to it, but the Sn(1)-Ir(1) vector lies 35° out of the equatorial plane toward Br(1). The two Sn-Br bond lengths show a marked difference; the Sn(1)-Br(1) bond, asso-ciated with bonding to Ir(1), is much longer than Sn(1)-Br(2) [2.934 (1) versus 2.608 (1) Å]. The latter distance is closer to, but somewhat shorter than, the normal range of 2.63-2.68 Å found for axial Sn-Br bonds in pentacoordinated tin compounds with trigonal bipyramidal geometries.[14]

Geometry of the Iridium-Tin Interaction. The salient feature of the structure of **2** is the rather regular triangle formed by Ir(1), Sn(1), and Br(1) [Sn(1)-Ir(1)-Br(1) = 68.51 (3), Ir(1)-Br-(1)-Sn(1) = 56.52 (3), and Ir(1)-Sn(1)-Br(1) ; 54.97 (3)°]. The Ir-Sn distance of 2.6297 (8) Å lies within the normal range for single Ir-Sn bonds (2.59-2.64 Å).[13d,e,15] The Ir-Br distance of 2.582 (1) also lies within the normal range of 2.52-2.64 Å found for this bond.[16] The triangular geometry of the Ir-Sn-Br unit closely resembles that of M-Sn-X units in three other group 6 metal d^6 complexes, i.e., (2,2'-bipyridine)(CO)$_3$Mo(Cl)SnMeCl$_2$ (**8a**),[17a] [MeS(CH$_2$)$_2$SMe](CO)$_3$W(Cl)SnMeCl$_2$ (**8b**),[17b] and [MeS(CH$_2$)$_2$SMe](CO)$_3$Mo(Cl)SnCl$_3$ (**8c**),[17c] whose common structural features are depicted in Table VI. The striking geo-metrical similarities suggest that a common mode of bonding exists between the transition metal and tin fragments in all four species (see Discussion).

Stability of [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(X)SnRR'X (1-6) and Reactions of Ir[C$_6$H$_3$(CH$_2$NMe$_2$)-2-R-6](COD) (R = Me, CH$_2$NMe$_2$) with SnMe$_2$Br$_2$. All adducts **1-6** are indefinitely stable in the solid state, while adducts **3** and **6** (which bear *no* Sn-Me bonds) are also stable in solution, even in the presence of a large excess of a coordinating solvent like pyridine. However, the other adducts **1**, **2**, **4**, and **5** (which do bear Sn-Me bonds) decompose within 1 day in either dichloromethane or benzene solutions. The decomposition of these complexes, which is a first-order process ($t_{1/2}$ ≅ 10 h), results in the simultaneous formation of C$_6$H$_5$CH$_2$NMe$_2$ and [IrX(COD)]$_2$, together with some off-white precipitate (eq 3). On the basis of the products left in solution,

$$[2-(\text{Me}_2\text{NCH}_2)\text{C}_6\text{H}_4](\text{COD})\text{Ir(X)SnMeRX} \rightarrow$$
$$\text{C}_6\text{H}_5\text{CH}_2\text{NMe}_2 + \frac{1}{2}[\text{IrX(COD)}]_2 + \text{``Sn(CH}_2\text{)RX''} \quad (3)$$

the insoluble precipitate must contain all of the tin and has the stoichiometry [Sn(CH$_2$)RX]$_n$. This material is possibly a polymer analogous to carbosilanes. For the formation of C$_6$H$_5$CH$_2$NMe$_2$ a hydrogen atom appears to be abstracted from an Sn-Me group of the starting iridium-tin adduct, since only those adducts bearing Sn-Me groups are prone to this decomposition. The mechanism of this reaction is unknown but could involve a kind of β-elimi-

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**Table VI.** Selected Geometrical Data of 2 and 8a-c[17][a]

compound	Sn-M-X$_{ax}$ triangle			X$_{ax}$-(Sn)-X$_{ax'}$ axis		
	Sn-M-X$_{ax}$	M-X$_{ax}$-Sn	X$_{ax}$-Sn-M	X$_{ax}$-Sn-X$_{ax'}$	Sn-X$_{ax}$	Sn-X$_{ax'}$
(2) [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(Br)SnMe$_2$Br	68.26 (4)	56.59 (4)	55.15 (3)	170.88 (5)	2.933 (2)	2.626 (2)
(8a) (2,2'-bipyridine)(CO)$_3$Mo(Cl)SnMeCl$_2$	63.6 (1)	61.6 (1)	54.8 (1)	168.1 (1)	2.805 (4)	2.433 (5)
(8b) (MeSCH$_2$CH$_2$SMe)(CO)$_3$W(Cl)SnMeCl$_2$	68.0 (2)	59.9 (2)	52.1 (2)	165.9 (3)	2.96 (1)	2.38 (1)
(8c) (MeSCH$_2$CH$_2$SMe)(CO)$_3$Mo(Cl)SnCl$_3$	64.3 (1)	60.5 (1)	55.2 (1)	172.9 (2)	2.781 (4)	2.381 (5)

[a] Bond angles in deg; bond lengths in Å. X$_{ax}$ is the tin-bonded axial halide that is also involved in bonding to either Ir, Mo, or W.

Scheme I
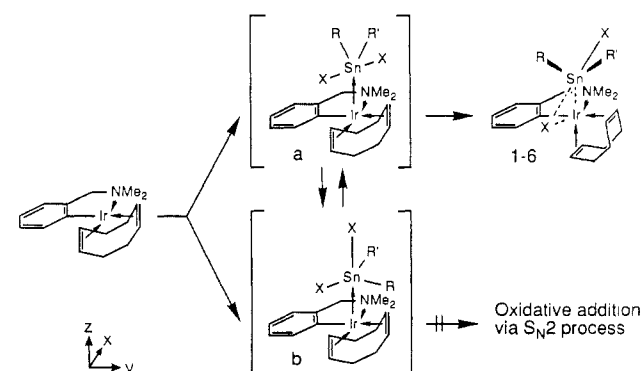
nation process of an Ir-Sn-CH$_3$ moiety, affording "Sn(CH$_2$)RX" and the intermediate IrHX[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) (eq 4).
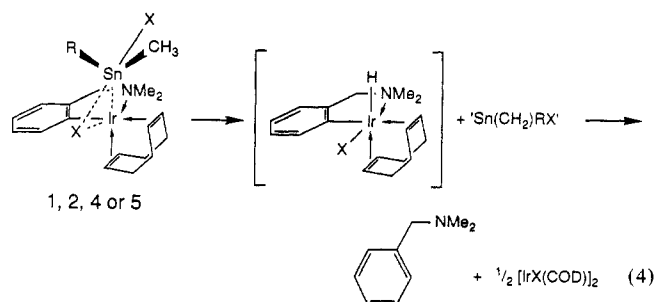
The bis-ortho-substituted aryl complexes Ir[C$_6$H$_3$-(CH$_2$NMe$_2$)-2-R-6](COD) (R = Me, CH$_2$NMe$_2$) were also reacted with SnMe$_2$Br$_2$ in benzene. In these cases, no formation of Ir-Sn adducts was observed, but instead an instant decomposition to 1-(Me$_2$NCH$_2$)-3-R-C$_6$H$_4$ and [IrBr(COD)]$_2$ occurred (100% for R = Me, 65% for R = CH$_2$NMe$_2$). Apparently the same decomposition pathway is followed as for the mono-ortho-substituted complexes. However, the reaction time (a few seconds) is much shorter and must be due to the steric crowding that the R-group exerts in the presumed intermediate [6-R-2-(Me$_2$NCH$_2$)C$_6$H$_3$](COD)Ir(Br)SnMe$_2$Br.

For R = CH$_2$NMe$_2$ a competing transmetalation reaction occurred, resulting in 35% formation of {SnMe$_2$[C$_6$H$_3$-(CH$_2$NMe$_2$)$_2$-2,6]}Br. In this respect, it is noted that the related complex Rh[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) is known to react with SnMe$_2$Br$_2$ to afford 100% {SnMe$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]}Br (eq 5).[7] This transmetalation reaction is thought to proceed via

Rh[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6](COD) + SnMe$_2$Br$_2$ →

{SnMe$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]}Br + $^1/_2$[RhBr(COD)]$_2$ (5)
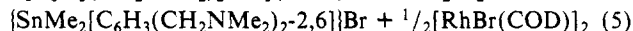
electrophilic attack of the tin moiety on the Rh-C bond or on the C(aryl) atom but *not* on the rhodium center. In contrast, the similar reaction with the iridium complex appears to proceed mainly via the iridium center, i.e., by the intermediate formation of an Ir-Sn adduct and concomitant decomposition. This difference in behavior must, therefore, be attributed to the higher nucleophilicity of iridium with respect to rhodium.

Discussion

Formation of [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(X)SnRR'X (1-6). The starting complexes Ir[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) and SnRR'X$_2$ have a square-planar and a tetrahedral geometry around the metal, respectively, but both end up as trigonal bipyramids
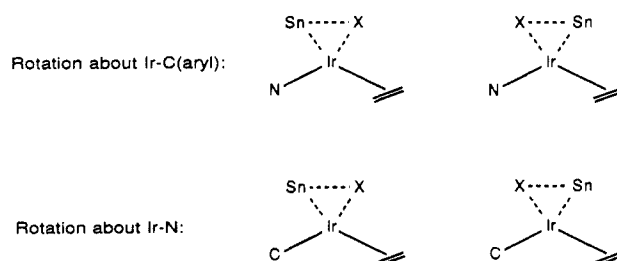

Figure 3. Possible stereoisomers of [2-(Me$_2$NCH$_2$)C$_6$H$_4$](COD)Ir(X)-SnRR'X (1-6).

in the final products 1-6. In discussing the consequences of these geometrical changes from an MO point of view, the x and y axes are taken as approximately colinear with the respective Ir-N and Ir-C(aryl) bonds of the starting iridium(I) complex, and the z axis is perpendicular to the coordination plane (Scheme I).

The First Step. The primary interaction of SnRR'X$_2$ with the iridium center of Ir[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) occurs along the z axis and can take place through either a halide atom, a tin-halide bond, or the tin atom. The first two possibilities are seen to be unlikely because the HOMO of the starting iridium(I) complex, being a mainly metal localized d$_{z^2}$ orbital, will encounter a strong anti-bonding interaction with filled orbitals of the same symmetry on the tin species. Therefore, the primary interaction is likely to be of a Lewis acid-base type through the filled d$_{z^2}$ orbital of iridium and an empty orbital of tin, see Scheme I. This is corroborated by the experimental observation that on increasing the number of halide atoms on tin, and hence the Lewis acidity of the tin(IV) center, the adduct formation proceeds more readily. This type of interaction would also explain why the weaker Lewis acid SnMe$_3$Cl does not form an adduct under the conditions employed.

In order to bond with the iridium complex, the tin species has to rehybridize from a tetrahedral (sp^3) to a trigonal bipyramidal (sp^{3}d) arrangement by admixture of an empty 5d orbital. The bonding of the five-coordinate tin center will then be directed in such a way as to accommodate the more electronegative atoms (halide atoms) in axial and the better σ-donor (iridium atom) in equatorial positions.[18] At the same time the coordination around iridium will change toward square pyramidal. Two intermediate structures, differing by their arrangement of tin-bonded substituents, can be put forward (a and b in Scheme I). This difference is of minor importance, since for following steps these structures can probably interchange readily via low barrier, Berry rotations around the tin atom.[19] Although structure b appears well suited to react further by means of an S$_{N}$2 type oxidative addition process, involving breakage of the axial tin-halide bond, it does not do so. This process, however, probably does operate in the trans oxidative addition of a tin-halide bond of SnR$_3$X to the metal d^8 complex Pt^{II}Me$_2$(N-N) (N-N = 2,2'-bipyridine and 1,10-phenanthroline).[20] Stable dinuclear metal d^8→d^{10} Lewis acid-base adducts of the type described above have not as yet been reported with tin(IV) compounds, but they are known with mercury(II) salts, e.g., [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]Pt[μ-(p-tol)NC-(H)N(i-Pr)]HgBrCl.[21]

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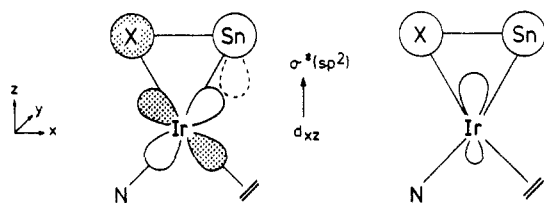
Figure 4. Bonding interaction between the iridium and tin moieties in [2-(Me₂NCH₂)C₆H₄](COD)Ir(X)SnRR'X (1-6).

The Second Step. The bonding between the iridium and tin moieties in the final products 1-6 is clearly different from that in the preceding Lewis acid-base adduct, described above. It seems likely that starting from this initial interaction a concerted process takes place in which the iridium moiety migrates from tin toward the tin-halide bond. As such this migration can be regarded as the first stage of a concerted cis oxidative addition of a tin-halide bond to an iridium(I) center, and the present complexes (1-6) can therefore be considered as "trapped" intermediates in this process.

This migration can, in principle, give rise to four stereoisomers, although only one is observed (Figure 3). Firstly, to enable coordination of a tin-halide bond to iridium, rotation of the aryl ligand (in the xz plane, z intersecting the vector of the rotating ligands) about the Ir-C(aryl) axis occurs and *not* about the Ir-N axis. This exclusive rotation about Ir-C(aryl), also realized during the reaction of Ir[C₆H₄(CH₂NMe₂)-2](COD) with dihydrogen,[6] seems to be directed by repulsive forces within the complex. Secondly, although the iridium-coordinated tin-halide bond can in principle orient itself in two ways in the equatorial (xz) plane, the tin atom is directed opposite to the in-plane N atom, which has a larger trans influence than the COD double bond.

Upon migration of the iridium moiety toward a tin-halide bond the amine group and the other COD double bond bend ca. 65° toward each other, resulting in the formation of a bent d⁸ ML₄ arrangement. This bending destabilizes the d_{xz} orbital of iridium, which now becomes the HOMO of the iridium moiety, and stabilizes the d_{z^2} orbital. While the donative interaction of the d_{z^2} orbital with a tin sp² hybrid decreases, the π-interaction of the d_{xz} orbital with the σ* orbital of the tin-halide bond increases (it is possible that this tin sp² hybrid, pointing more or less toward iridium, remains involved in the bonding in the final adduct) (Figure 4). In this respect, it should be recalled that the coordinated Sn-X bond in the adducts 1-6 (cf. Sn-Br in the X-ray structure of 2) lies approximately in the equatorial (xz) plane, an orientation that is calculated to be optimal for π-overlap.[21] Additionally, the LUMO of the bent iridium moiety, being an orbital of approximate sp² symmetry, can, in a kind of "backbonding", accept electrons from the σ orbital of the tin-halide bond (Figure 4). The final bonding description is very similar to that of the classical example of the interaction of an olefin with the bent Fe(CO)₄ fragment,[22] whose frontier orbitals are isolobal with the bent Ir[C₆H₄(CH₂NMe₂)-2](COD) moiety.

Except for the side-on coordinated hydrogen molecule, the σ and σ* orbitals of diatomic substrates in general lie respectively too low and too high in energy for a significant overlap with metal orbitals.[23] However, in the present case it can be anticipated that the rehybridization of tin orbitals upon changing from a tetrahedral to a trigonal bipyramidal geometry will produce weakened axial bonds and so bring the σ and σ* orbitals closer in energy to the frontier orbitals of iridium.

The Third Step. Starting from the adducts 1-6, oxidative addition of the tin-halide bond (i.e., formation of two Ir-X and Ir-Sn single bonds) is expected to be the next reaction step. The fact that this does not happen, in contrast to a number of other cases,[3,18,24] may be ascribed in part to steric crowding. This

explanation was also put forward for the formation of the complexes (LL)(CO)₃M(X)SnRR'X (8a-c, LL = bidentate S or N ligand, M = Mo, W) that contain a nearly identical M-Sn-X triangle, from M(LL)(CO)₄ and SnRR'X₂.[17] However, factors other than those of steric origin must also play a role since in other similar cases, such as the reaction of W(2,2'-bipyridine)(CO)₄ with GeBr₄, a true seven-coordinate oxidative addition product *does* form.[25] As observed earlier, there are striking structural similarities, regarding the M-Sn-X triangles (Table VI), between our iridium-tin adducts (1-6) and the molybdenum/tungsten-tin adducts (8). Since the transition-metal fragments involved in these adducts (bent d⁸-ML₄ in 1-6 and d⁶-ML₅ in 8) are isolobal, it is to be expected that common electronic factors govern the choice between side-on coordination or oxidative addition of the tin-halide bond.

This choice has recently been discussed in a quantitative way for dihydrogen, for which both examples of η² coordination and oxidative addition are known.[26] Ab initio studies on the WL₅H₂ system showed that reduced π overlap between the metal d_{xz} and the dihydrogen σ* orbital prevents oxidative addition and hence stabilizes side-on coordination of dihydrogen instead. In the present iridium-(and molybdenum/tungsten-)tin complexes it can be argued that a similar overlap "imbalance" exists between the frontier orbitals of the transition metal and the σ and σ* orbitals of the Sn-X bond, for which there is little σ and π synergistic interaction that would drive the system to concerted cis oxidative addition.

Another factor of relevance in the discussion of the M-Sn-X triangle is the significant degree of π-character in a tin-halide bond arising from donation of filled p orbitals of the halide atoms to empty 5d orbitals on tin.[27] Although this interaction is relatively weak, compared to that of the σ-bond, it is possible that in 1-6 and 8 it is just this extra tin-halide bonding, which stabilizes (in cooperation with steric factors) the three-center M-Sn-X interaction with respect to an oxidative addition product.

More Analogies. The iridium moiety in 1-6, being a bent d⁸ ML₄ fragment, is not only isolobal with the d⁶ ML₅ fragment (as in 8) but also with T-shaped d⁸ ML₃, bent d¹⁰ ML₂, and the methylene group.

The mechanism of the cis oxidative addition of tin-halide bonds to several platinum(0) complexes of the bent d¹⁰ ML₂ type[24] may well involve an intermediate having a Pt-Sn-X triangle analogous to that in 1-6 and 8.

From the isolobal point of view, the tin(IV) compounds Sn-(CH₂X)R₃, which bear a methyl group α-substituted by a halide atom are also interesting. These compounds are thought to possess intramolecular coordination of the halide X to tin,[28] but this situation can also be regarded as an example of a tin-halide bond that is side-on coordinated to a methylene group.

As well as tin, other group 14 elements can be involved in side-on bonding. For example, complexes of the type Cp-(CO)₂Mn(H)SiRR'R", in which the Si-H bond acts as side-on coordinated ligand, can be regarded as "trapped" intermediates in hydrosilylation reactions.[29] However, in contrast to the tin atom in 1-6 (and 8), the silicon atom in these manganese complexes are found to be tetrahedral. Finally, the analogy that exists between side-on coordinated Sn-X and Si-H bonds and agostic C-H bonds should be mentioned,[30] especially in the light of the

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recent detection of η^2-coordinated C–H bonds by Bergman et al.[31]

Conclusions

The special arrangement of ligands in square-planar Ir-[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD) has resulted in the isolation of unique adducts with organotin(IV) halides that can be regarded as "trapped" three-center intermediates in the oxidative addition of a metal–halide bond to metal d^8 complex. It can be anticipated, based on isolobal relationships, that many new transition-metal complexes having side-on coordinated (main group) M–X bonds can be synthesized not only with tin(IV) (or other group 14 elements) but also with d^{10} metals like thallium(III), mercury(II), and gold(I).

Registry No. 1, 115076-05-6; **2**, 115076-06-7; **3**, 115076-07-8; **4a**, 115076-08-9; **4b**, 115116-29-5; **5**, 115076-09-0; **6**, 115076-10-3; Ir-[C$_6$H$_4$(CH$_2$NMe$_2$)-2](COD), 114762-91-3; SnMe$_2$Cl$_2$, 753-73-1; SnMe$_2$Br$_2$, 2767-47-7; SnPh$_2$Cl$_2$, 1135-99-5; SnMePhBr$_2$, 21247-36-9; SnMeCl$_3$, 993-16-8; SnBr$_4$, 7789-67-5; [IrBr(COD)]$_2$, 12245-73-7; [C$_6$H$_5$CH$_2$NCH)Me$_2$]Cl, 1875-92-9; Ir[C$_6$H$_3$(CH$_2$NMe$_2$)-2-Me-6]-(COD), 114762-90-2; Ir[C$_6$H$_3$(CH$_2$NMe$_2$)-2-CH$_2$NMe$_2$-6](COD), 114762-89-9; [1-(Me$_2$(H)NCH$_2$)-3-Me-C$_6$H$_4$]Cl, 115031-97-5; [1,3-(Me$_2$(H)NCH$_2$)$_2$C$_6$H$_4$]Cl$_2$, 63400-16-8; {SnMe$_2$[C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6]}Cl, 115092-11-0.

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Defect Patterns in Perovskites

Jeremy K. Burdett* and Gururaj V. Kulkarni

Contribution from the Chemistry Department, The University of Chicago, Chicago, Illinois 60637. Received December 9, 1987

Abstract: The method of moments is used to understand the results of molecular orbital calculations and tight-binding calculations on solids, designed to probe the reasons behind the ordering problem of defects in solids. This is a problem that can be regarded as the solid-state equivalent of the isomerization question in molecular chemistry. The structural preferences for *cis*- and *trans*-dioxo transition-metal complexes and the "defect patterns" predicted for binuclear vertex-sharing octahedral complexes of stoichiometry M$_2$L$_9$ are used to build a simple model that may be easily applied to the case of transition-metal-containing perovskites. The calculations and the model give a ready explanation for the observed ordering pattern in CaMnO$_{2.5}$ and defect structures with fewer oxygen vacancies.

One of the important aspects of the geometrical structure of molecules is, of course, the stability of isomers of various types. Rotational isomerism in organic chemistry and the relative stability of cis and trans isomers in transition-metal chemistry come immediately to mind. Often the stability of the two structures varies with electron count. For example, *cis*-dioxo complexes are exclusively found for d^0 metal centers but the trans isomer for d^2 systems. Often the predicted properties of the two isomers are very different, and this point underscores the often striking dependence of properties on structure. Seemingly minor geometrical variations often lead to very different properties.

Ordering patterns in molecules are important too. Given a collection of atoms that are to be assembled into a molecule of a set shape, what influences the choice of atomic connectivity? For example, in the structure of nitrous oxide, the oxygen atom is found in a terminal rather than central position. The most stable "coloring" pattern changes too with electron count. In the A$_2$O oxides, for molcules with 8–12 electrons (Li$_2$O, Ga$_2$O, for example) the oxygen atom is centrally located in contrast to the 16-electron case of N$_2$O.

In this paper we will study a problem of very basic chemical importance in the condensed phase. We will present a theoretical way to understand the ordering patterns of defects in solids. Our model will be applied initially to systems derived from the perovskites, materials of composition ABO$_3$.[1] Such defect structures give us a solid-state equivalent of the isomerism problem of the molecular chemist. Here we wish to understand what influences

their relative stabilities. Throughout our analysis we shall make extensive analogies with molecular problems. The major thrust in this paper will be to understand the atomic arrangement in the material CaMnO$_{2.5}$ and other related systems with slightly higher oxygen content. Elsewhere we extend the picture to structures with lower oxygen content (O$_{2.33}$), which have recently been found to be high T$_c$ superconductors.[2-4] We will use one-electron orbital models which have proven immensely useful in almost all areas of chemistry, and will find the method of moments especially useful in understanding the variation in structural stability with electron count.

Defects in CaMnO$_3$

The chemist's view of defect structures is one that has changed over the years.[5-7] Many of the structures, that carried this label years ago are now recognized as chemically distinct phases. If the number of defects is rather small (such as the Schottky defects

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