$C_5Me_5)Ir(CO)_2$ and $W(CO)_6$. Likewise with PPh_3, 1 gave $W(CO)_5(PPh_3)$. (The products in each case were identified by infrared spectroscopy.) These reactions are consistent with the slow dissociation of 1 into $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ and $W(CO)_5$, in solution at room temperature. The decomposition of 1, mentioned earlier, is also typical of labile $LW(CO)_5$ complexes.[19] The dissociation of 1 (and reaction with PPh_3) may be compared to that of the recently reported species $(\mu\text{-}H)[Fe(CO)_4W(CO)_5]^-$[20] and $(OC)_5Os\text{-}Ru(CO)_3(SiCl_3)(Br)$.[21] The latter molecule, which contains an Os–Ru dative bond, rapidly dissociates in solution to give an equilibrium mixture with significant concentrations of $Os(CO)_5$ and $[Ru(CO)_3(SiCl_3)(Br)]_2$.

When 1 was stirred in solution with $Os(CO)_4(PMe_3)$, $(Me_3P)(OC)_4OsW(CO)_5$[1] was formed in about the same time period as that required to effect the substitutions described above. In contrast there was no reaction of $(Me_3P)(OC)_4OsW(CO)_5$ with $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$ under the same conditions. From these experiments it may be concluded that $Os(CO)_4(PMe_3)$ is a stronger donor ligand than $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.[22]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the President's Research Fund (Simon Fraser University) for financial support. We also wish to thank Dr. J. K. Hoyano and Professor W. A. G. Graham (University of Alberta) for details of the preparation and crystal structure of $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$.

Registry No. $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$, 92543-25-4; $W(CO)_5(THF)$, 36477-75-5; $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, 32660-96-1; Ir, 7439-88-5; W, 7440-33-7.

Supplementary Material Available: Tables of atomic coordinates for hydrogen atoms, bond lengths and angles involving hydrogen atoms, least-squares planes, and final temperature factors, and a structure factor listing for $(\eta^5\text{-}C_5Me_5)(OC)_2IrW(CO)_5$ (35 pages). Ordering information is given on any current masthead page.

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(22) The W–C bond length trans to osmium in $(Me_3P)(OC)_4OsW(CO)_5$ (1.964 (8) Å)[1] is longer than the corresponding distance in 1 (1.940 (8) Å). Although this is consistent with the view that $Os(CO)_4(PMe_3)$ is a better donor ligand than $(\eta^5\text{-}C_5Me_5)Ir(CO)_2$, the difference in the two lengths is not statistically significant.

X-ray Crystal and Molecular Structure of Bis(biphenylyl-2)tin(IV) Dichloride, a Discrete, Molecular, Organotin Chloride

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Bis(biphenylyl-2)tin(IV) dichloride forms clear, diamond-shaped, monoclinic crystals, mp 165–166 °C, in the space group $P2_1/n$ with a = 13.039 (5) Å, b = 14.173 (4) Å, c = 11.478 (4) Å, β = 90.83 (3)°, V = 2120.8 (12) Å^3, Z = 4, and ρ_{calcd} = 1.553 g cm^{-3}. The structure was determined from 4503 reflections collected on a Syntex P3 automated diffractometer with monochromatic Mo Kα radiation (λ_α = 0.71069 Å) and refined to a final R value of 5.0% for the 2754 reflections included in the least-squares sums. The monomeric molecules are well separated in space with the nearest Cl···Sn contacts at 6.189 (3) Å. The title compound is thus the first tin dihalide to form a monomeric solid. The angles at the badly distorted tetrahedral tin(IV) atom are in the expected order Cl(1)–Sn–Cl(2) [99.71 (9)°] < Cl(1)–Sn–C(13) = Cl(2)–Sn–(1) [104.0 (2)°] < Cl(2)–Sn–C(13) [106.5 (2)°] ≈ Cl(1)–Sn–C(1) [107.8 (2)°] < C(1)–Sn–C(13) [130.8 (3)°], but the compression of the first and the widening of the last, which are more typical of a higher coordinated, chloride-bridged structure, are in this case produced by the steric requirements of the bulky organic ligand.

Organotin chlorides are crossroads materials, centrally poised among trends to higher coordinated, bridged structures: descending the fourth group, carbon to lead; ascending the seventh group, iodine to fluorine; increasing the number of halide substituents, zero to four; or reducing the steric demand of the organic ligands. Among the diorganotin dichlorides themselves there are discrete monomers (gas-phase and solution) and chlorine-bridged solids,[1,2] the latter employing single chlorine atoms linking five-coordinated tins or two chlorine atoms linking six-coordinated tins by chelation of one molecule by its neighbor or employing a more symmetrical mode in which trans octahedral chlorines on each molecule bridge. Validation of higher coordination at the central tin atom or bridging by attached chlorines demands analysis of often ambiguous solid-state structural data in terms of potentially coordinating halogen atoms lying in stereochemically significant positions[3] at short intermolecular contact distances. For the evidence to be truly compelling, angle distortions and bond length increases must be significantly greater than those produced by packing forces or the operation of steric or bonding (isovalent rehybridization) effects in the monomers themselves. Benchmark data are

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provided by gas-phase studies (electron diffraction or microwave) and by the structures of compounds that crystallize as discrete monomers.

Examples of bridged organotin chlorides include (η^5-cyclopentadienyl)tin(II) chloride,[4] η^5-C_5H_5SnCl, first made by one of us[5] in 1969, dimethyltin(IV) dichloride, $(CH_3)_2SnCl_2$, which forms double, unsymmetrical chlorine–tin bridges with methyl groups projecting above and below the Sn_2Cl_2 plane,[6] trimethyltin(IV) chloride, $(CH_3)_3SnCl$, which one of us showed contains chlorine atoms bridging planar trimethyltin units,[7] bis(chloromethyl)tin(IV) dichloride, $(ClCH_2)_2SnCl_2$, in which one molecule's $SnCl_2$ system chelates the next,[8] diethyltin(IV) dichloride,[9] $(C_2H_5)_2SnCl_2$, which resembles its methyl homologue,[6] and diphenyltin(IV) dichloride, $(C_6H_5)_2SnCl_2$, in which considerable distortion from tetrahedral geometry is observed. The original authors interpreted the structure as a system of discrete monomers,[10] but a subsequent reinterpretation argues that the solid consists of chains of four molecules with end members containing four-coordinated and the two interior molecules containing six-coordinated tin atoms. The former serve as donor chlorine bridges only, while the latter participate as acceptors from the terminal molecules and both donors and acceptors to each other.[8] Finally, solid triphenyltin(IV) chloride, $(C_6H_5)_3SnCl$, contains genuinely discrete, monomeric molecules.[11,12]

This paper reports the structure of bis(biphenylyl-2)-tin(IV) dichloride,[13,14] (2-$C_6H_5C_6H_4)_2SnCl_2$, the first example of a tin dihalide to form a completely monomeric solid.

Experimental Section

The title compound, a known material from the HCl cleavage of 9,9′-spiro-bis[dibenzostannol],[13,14] was the fortuitous product of the following procedure.

n-Butyllithium in hexane (20 mL, 2.3 M, 46.0 mmol) (Alpha Inorganics) diluted with ether dried by distillation from $LiAlH_4$ just before use (20 mL) was added dropwise under nitrogen over 2 h to 2,2′-dibromobiphenyl[15] (7.18 g, 23.0 mmol) in ether (100 mL) at room temperature and the mixture stirred for an additional 2 h. The mixture was then added dropwise over 3.5 h to phenyltin(IV) trichloride distilled just prior to use (13.94 g, 46.1 mmol) in ether (100 mL) at reflux and refluxing was continued overnight. Filtration and distillation of the filtrate in vacuum finally gave a tan syrup as the last fraction. This material was recrystallized from 1:1 CH_2Cl_2 and methanol to yield 0.41 g of the title compound,[13,14] mp 165–166 °C (lit.[13] mp 170.0–170.5 °C, lit.[14] mp 169.5–170.5 °C). Anal. Calcd for $C_{24}H_{18}Cl_2Sn$: C, 58.12; H, 3.66; Cl, 14.30; Sn, 23.93. Found: C, 56.25; H, 3.66; Cl, 14.35; Sn, 21.73.

The colorless, diamond-shaped crystals were soluble in $CHCl_3$, CH_2Cl_2, THF, and ether but were insoluble in methanol and ethanol. Slight sensitivity to air and moisture was observed.

Table I. Crystal Data for Bis(biphenylyl-2)tin(IV) Dichloride ((2-$C_6H_5C_6H_4)_2SnCl_2$)[a]

formula	$C_{24}H_{18}Cl_2Sn$
fw	496.00
a, Å	13.039 (5)
b, Å	14.173 (4)
c, Å	11.478 (4)
β, deg	90.83 (3)
V, Å^3	2120.8 (12)
F(000)	984
μ(Mo Kα), cm^{-1}	4.68
λ(Mo Kα), Å	0.710 69
ρ_{calcd}, g cm^{-3}	1.553
Z	4
obsd reflctn	2754
R	5.0%
space group	$P2_1/n$
cryst dimens, mm	0.2 × 0.25 × 0.35

[a] Estimated standard deviations in parentheses.

Spectroscopic data include tin-119m Mössbauer (77 K), mm s^{-1}: IS = 1.42 ± 0.03; QS = 2.73 ± 0.06; Γ_1 = 1.18 ± 0.3; Γ_2 = 1.02 ± 0.03 (ρ = QS/IS = 1.92) (recorded on a Ranger-Engineering spectrometer equipped with an NaI scintillation counter and using $Ca^{119m}SnO_3$ as source and standard reference material for zero velocity. Velocity calibration was based upon β-tin and natural iron foils). NMR ($CDCl_3$ vs. Me_4Si): ^1H, 7.43, 7.39, 7.37, 7.16 ppm; ^{13}C, 143.4, 141.1, 135.5, 135.3, 131.2, 130.0, 129.6, 129.3, 128.7, 127.8 ppm (recorded on an IBM NR-80 instrument). Mass spectrum (12 eV): *m*/*e* (fragment, relative abundance) 538 ($[C_6H_6C_6H_4)_2SnC_6H_5Cl]^{+\cdot}$, 2.8), 501 ($[C_6H_5C_6H_4)_2SnC_6H_5 - 2H]^+$, 4.4), 496 ($[(C_6H_5C_6H_4)_2SnCl_2]^{+\cdot}$, 8.8), 460 ($[(C_6H_5C_6H_4)_2SnCl - H]^{+\cdot}$, 18.1), 424 ($[(C_6H_5C_6H_4)_2Sn - 2H]^{+\cdot}$, 1.2), 383 ($[C_6H_5(C_6H_4)_3C_6H_5 - H]^{+\cdot}$, 1.6); 343 ($[C_6H_5C_6H_4SnCl_2]^+$, 3.9), 305 ($[C_6H_5(C_6H_4)_2C_6H_5]^+$, 100.0), 228 ($[C_6H_5C_6H_4C_6H_5 - 2H]^{+\cdot}$, 154 ($[C_6H_5C_5H_5]^{+\cdot}$, 2.5) (recorded on a Hewlett-Packard 5985B spectrometer; mass numbers are based upon ^1H, ^{12}C, ^{35}Cl, and ^{120}Sn). Infrared and Raman data, 4000–170 cm^{-1}, are deposited with the supplementary material as Table SI.

Data Collection and Structure Determination

Unit-cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using Mo radiation (λ = 0.71069 Å). Data (4776 points) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 116°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less than 8% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects, but not for absorption effects. After removal of redundant (182) and space group forbidden (91) data, 4503 data points remained of which 2754 reflections were considered observed [$I > 3.0\sigma(I)$]. The structure was solved from a Patterson synthesis to locate the heavy atom. Successive least-squares/difference-Fourier cycles allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor and positional and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Hydrogen positional parameters were determined from a difference-Fourier synthesis.[16] These hydrogen positional parameters and the associated isotropic thermal parameters were refined along with non-hydrogen parameters in the final cycles of refinement. The final cycle of refinement [function minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor, R = 5.0% [$R = (\sum||F_o| - |F_c||/|F_o|) \times 100$]. Anomalous dispersion corrections were made for Sn and Cl. Scattering factors were taken from ref 17. Unit weights were used throughout.

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Table II. Positional Parameters for Bis(biphenylyl-2)tin(IV) Dichloride ($(2\text{-}C_6H_5C_6H_4)_2SnCl_2$)[a]

atom	*x*	*y*	*z*
Sn1	1.0976 (0)	0.1894 (0)	0.1973 (1)
Cl1	1.1342 (2)	0.1219 (2)	0.3842 (2)
Cl2	1.1037 (2)	0.3525 (2)	0.2468 (2)
C1	0.9391 (7)	0.1643 (6)	0.1573 (8)
C2	0.8780 (8)	0.2408 (8)	0.1301 (10)
C3	0.7734 (9)	0.2264 (10)	0.1105 (11)
C4	0.7312 (8)	0.1386 (11)	0.1214 (11)
C5	0.7923 (8)	0.0627 (9)	0.1497 (10)
C6	0.8986 (7)	0.0736 (7)	0.1680 (8)
C7	0.9635 (7)	−0.0092 (7)	0.2013 (8)
C8	0.9386 (8)	−0.0654 (8)	0.2953 (9)
C9	1.0037 (9)	−0.1374 (8)	0.3302 (10)
C10	1.0910 (9)	−0.1554 (8)	0.2687 (10)
C11	1.1154 (7)	−0.1028 (7)	0.1740 (9)
C12	1.0532 (7)	−0.0284 (6)	0.1385 (8)
C13	1.2311 (6)	0.1612 (6)	0.1001 (7)
C14	1.3005 (7)	0.0921 (7)	0.1389 (8)
C15	1.3922 (7)	0.0789 (8)	0.0884 (9)
C16	1.4182 (8)	0.1329 (8)	−0.0042 (10)
C17	1.3542 (8)	0.2038 (8)	−0.0455 (9)
C18	1.2581 (7)	0.2180 (6)	0.0063 (8)
C19	1.1903 (7)	0.2956 (7)	−0.0363 (8)
C20	1.0901 (8)	0.2769 (8)	−0.0740 (9)
C21	1.0278 (9)	0.3504 (10)	−0.1113 (10)
C22	1.0638 (11)	0.4408 (9)	−0.1103 (11)
C23	1.1625 (11)	0.4612 (9)	−0.0732 (12)
C24	1.2262 (9)	0.3892 (8)	−0.0368 (10)

[a] Estimated standard deviations in parentheses.

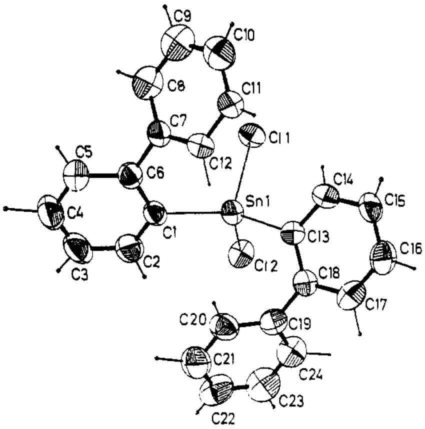

Figure 1. Bis(biphenylyl-2)tin(IV) dichloride showing the atomic numbering. The ring containing C(1)–C(6) is A, C(7)–C(12) is B, C(13)–C(18) is C, and C(19)–C(24) is D (see text).

Table III. Bond Distances (Å) and Angles (deg) for Bis(biphenylyl-2)tin(IV) Dichloride ($(2\text{-}C_6H_5C_6H_4)_2SnCl_2$)[a]

Bond Distances

Sn1–Cl1	2.391 (2)	C11–C12	1.39 (1)
Sn1–Cl2	2.381 (3)	C12–C7	1.41 (1)
Sn1–C1	2.140 (9)	C13–C14	1.40 (1)
Sn1–C13	2.119 (8)	C14–C15	1.35 (1)
C1–C2	1.38 (1)	C15–C16	1.36 (2)
C2–C3	1.39 (2)	C16–C17	1.38 (2)
C3–C4	1.37 (2)	C17–C18	1.41 (1)
C4–C5	1.38 (2)	C18–C13	1.39 (1)
C5–C6	1.41 (1)	C18–C19	1.49 (1)
C6–C1	1.40 (1)	C19–C20	1.40 (1)
C6–C7	1.49 (1)	C12–C21	1.38 (2)
C7–C8	1.38 (1)	C21–C22	1.36 (2)
C8–C9	1.38 (2)	C22–C23	1.38 (2)
C9–C10	1.37 (2)	C23–C24	1.38 (2)
C10–C11	1.36 (2)	C24–C19	1.41 (2)

Bond Angles

Cl1–Sn1–Cl2	99.71 (9)	C9–C10–C11	121.0 (10)
Cl1–Sn1–C1	107.8 (2)	C10–C11–C12	120.6 (9)
Cl1–Sn1–C13	104.0 (2)	C11–C12–C7	118.9 (8)
Cl2–Sn1–C1	104.0 (2)	Sn1–C13–C14	119.8 (6)
Cl2–Sn1–C13	106.5 (2)	Sn1–C13–C18	121.1 (6)
C1–Sn1–C13	130.8 (3)	C14–C13–C18	118.6 (8)
Sn1–C1–C2	118.1 (7)	C13–C14–C15	122.2 (9)
Sn1–C1–C6	119.9 (6)	C14–C15–C16	119.4 (10)
C2–C1–C6	121.8 (8)	C15–C16–C17	121.4 (10)
C1–C2–C3	118.8 (10)	C16–C17–C18	119.6 (9)
C2–C3–C4	120.8 (12)	C17–C18–C13	118.7 (8)
C3–C4–C5	120.1 (10)	C17–C18–C19	119.6 (8)
C4–C5–C6	121.0 (11)	C13–C18–C19	121.6 (8)
C5–C6–C7	120.4 (9)	C18–C19–C20	120.7 (9)
C5–C6–C1	117.4 (9)	C18–C19–C24	120.1 (9)
C1–C6–C7	122.2 (8)	C20–C19–C24	119.1 (10)
C6–C7–C8	120.9 (8)	C19–C20–C21	119.8 (11)
C6–C7–C12	119.5 (8)	C20–C21–C22	120.2 (12)
C8–C7–C12	119.6 (8)	C21–C22–C23	121.2 (12)
C7–C8–C9	120.1 (10)	C22–C23–C24	119.6 (11)
C8–C9–C10	119.8 (11)	C23–C24–C19	120.1 (11)

[a] Estimated standard deviations in parentheses.

Results

Crystal parameters are listed in Table I, atomic coordinates for non-hydrogen atoms in Table II, and bond distances and angles in Table III. Hydrogen atom positional parameters, anisotropic thermal parameters, equations of the planes, and listings of structure factors are available in the supplementary material. The molecular geometry and labeling scheme are given in Figure 1.

Description of the Structure

Bis(biphenylyl-2)tin(IV) dichloride crystallizes as a monomer with no significant intermolecular contact between tin and chlorine atoms [6.189 (3) Å minimum nonbonded distance]. The geometry of the tin atom is far from tetrahedral, however, with a greatly compressed Cl–Sn–Cl angle [99.71 (9)°] and a very wide C–Sn–C angle [130.8 (3)°]. The C–Sn–Cl angles are, as expected, intermediate, ranging from 104.0 (2)° for C(2)–Sn–Cl(1) and C(13)–Sn–Cl (2) to 107.8 (2)° for C(1)–Sn–C(1). This is precisely the order of angle size expected from the steric requirements of the ligands, $C_6H_5C_6H_4 > Cl$, or from isovalent hybridization considerations where the p character is concentrated in the bonds to the more electronegative groups resulting in angle closing $Cl < C_6H_5C_6H_4$. It would also have been anticipated if the molecules were either single chlorine bridged to give five-coordinate, trigonal-bipyramidal tin with equatorial organic groups and the bridging chlorine axial in the axially most electronegative arrangement or, alternatively, double chlorine bridged to form six-coordinate, octahedral tin with trans organic groups. However, the distortions wrought on the monomeric title compound are even more severe than in the several cases in which the geometry at tin has been hitherto rationalized by bridging interactions at long distances (see Table IV). Thus our results show that even large distortions from tetrahedral geometry can be brought about by ligand steric demand alone and hence cannot be used to confirm association by bridging atoms in the absence of other compelling evidence.

A direct comparison to our structure is available in diphenyltin(IV) dichloride,[10] but the interpretation of the data has been the subject of controversy.[8] The original authors debunked the claim of tin-119m Mössbauer spectroscopists who postulated intermolecular association on the basis of IS = 1.34 and QS = 2.16 mm s^{-1}.[23-26] But

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Table IV. Comparison Data for Organotin(IV) Chloride Structures[a]

compd	ref	d(Sn–C), Å	d(Sn–Cl), Å	∠C–Sn–C, deg	∠C–Sn–Cl, deg	∠Cl–Sn–Cl, deg	d(Sn···Cl), Å
$(2\text{-}C_6H_5C_6H_4)_2SnCl_2$, X-ray at room temp	b	2.119 (8) 2.140 (9)	2.381 (2) 2.391 (2)	130.8 (3)	104.0 (2) 104.0 (2) 106.5 (2) 107.8 (2)	99.71 (9)	6.189 (3)
$(C_6H_5)_2SnCl_2$, X-ray at room temp	8, 10	2.114	2.336 2.353 2.357	123.9 127.0	107	97.8 101.7	3.77 3.78
$(C_6H_5)_3SnCl$, X-ray at room temp	11	2.12	2.32	112.4	106.4		c
$(CH_3)_2SnCl_2$, X-ray at room temp	6	2.21	2.40	123.5	109.0	93.0	3.54
ed at 85–88 °C	17	2.108	2.327	c	109.8	107.5	
$(ClCH_2)_2SnCl_2$, X-ray at room temp	8	2.18	2.37	135	105	97	3.71
$(C_2H_5)_2SnCl_2$, X-ray at room temp	9	2.132 2.167	2.385 2.384	134.0	106.3	96.0	3.483 3.440
$(C_6H_5)_4Sn$, X-ray at room temp	19	2.144		108.8[d] 110.8[e]			
$(4\text{-}CH_3C_6H_4)_4Sn$, X-ray at room temp	20	2.147		107.0[d] 114.4[e]			
$(3\text{-}CH_3C_6H_4)_4Sn$, X-ray at room temp	21	2.150		109.54[d] 109.3[e]			
$SnCl_4$, ed at 0 °C	22		2.281			109.47	

[a] Standard deviations in parentheses. [b] This work. [c] Not given. [d] Fourfold. [e] Twofold.

their data were themselves subsequently reinterpreted in terms of a structure containing two different types of molecules in a tetrameric chain, the two outer members with four-coordinated and the two inner membranes with six-coordinated tin atoms forming an Sn_2Cl_2, double Cl-bridged ring. The terminal molecules are coordinated to the central pair by a Cl···Sn interaction of 3.78 Å, while the bridging chlorines in the central ring interact at 3.77 Å. These distances are the longest among the claimed associated diorganotin(IV) dichlorides listed in Table IV. Much of the departure from ideal tetrahedral geometry in the $(C_6H_5)_2SnCl_2$ solid must presumably arise from steric and bonding effects.

While no gas-phase structural data are available for $(C_6H_5)_2SnCl_2$, a direct test can be made for dimethyltin(IV) dichloride. Modern electron diffraction results[18] depict a molecule in which all the valence angles are near 109.5°, whereas in the solid state[6] the C–Sn–C angle is opened to 123.5° and the Cl–Sn–Cl angle closed to 93.0°. Trimethyltin(IV) chloride in the solid state is a chlorine-bridged, linear polymer[7] in which the C–Sn–C angles are opened to 117.1° and the C–Sn–Cl angles are closed to 99.9°, whereas the gas-phase molecules are more symmetrical[27] with C–Sn–C angles of 114.9° and C–Sn–Cl angles of 103.2°. Gas-phase data for other cognate systems are needed before definitive conclusions can be drawn.

It may be noted that the d(Sn–Cl) values in our structure are somewhat larger than those of the supposedly chlorine-bridged diphenyltin analogue[10] but then so are the d(Sn–C) values. In addition, the immediate coordination sphere about the tin atom appears, if anything, to be more distorted than in the diphenyltin analogue. The steric demand of the bulky 2-biphenyl ligand apparently has a weight equal to that of chlorine association in affecting the magnitude of the tin bond angles.

Our value of 1.49 (1) Å for the bond holding the two rings together in the biphenyl ligand compares to a range of 1.507[28]–1.493[29] Å found in the three X-ray[29,30] and one neutron[31] determination of the structure of biphenyl itself. However, covalent bonding to tellurium iodides (1.502,[32] 1.483[33] Å) or bromide[34] (1.474 Å) or adduct formation to antimony trichloride[35] (1.486 Å) might have been expected to shorten this connection.

The angles formed by the least-squares planes of the two pairs of directly connected biphenyl six-membered rings held by this C–C bond are 54.7° (rings A and C) and 60.3° (rings B and D). The corresponding angle formed by the two rings connected through the tin atom is 52.8° (rings A and B). The effect of this arrangement is to bring the ortho-carbon atoms on the outer rings, C(12) and C(20), into a short intramolecular contact with the tin atom at 3.210 (9) and 3.352 (11) Å, respectively. In the tellurium halide derivatives such short contacts (3.317 and 3.18 Å in the α- and β-forms of 2-biphenylyltellurium triiodide, respectively,[32,33] and 2.945 Å in the tribromide[34]) have a chemical implication, since heating 2-biphenylyltellurium or selenium halides eliminates HX at their melting points to form dibenzotelluro and selenophenes[32,36] containing a bond to the carbon making the short contact. In the case of our title compound, however, a sample held at 225 °C for 10 min still gives a reproducible melting point.

Tin-119m Mössbauer quadrupole splitting (QS) values generally increase with carbon–tin–carbon angles in diorganotin(IV) systems.[37] A treatment based upon a point-charge model yields a quantitative estimate of the magnitude of this angle in diphenyltin(IV) derivatives[38,39]

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using a partial QS value assigned for the phenyl group. Results are generally in accord with known structural data,[1,2,40] but exceptions are known.[41,42] The model assumes that there will be no QS sign inversion in the systems being compared and that the partial QS values for the ligands will be negligible compared to that of the phenyl group whose value must remain constant over the range of compounds studied. Some recorded QS values exceed those predicting linear C–Sn–C angles,[43,44] indicating breakdown of the model. No partial QS value is available for the biphenyl group, but using the value for phenyl yields 126.6° for the carbon–tin–carbon angle (vs. 130.8° measured), an error of only 4.2° or 3.2%.

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Supplementary Material Available: Tables of IR and Raman data, thermal parameters, hydrogen atom data, equations of planes, and structure factors (33 pages). Ordering information is given on any current masthead page.

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Structure and Reactivity of Bridging Dimanganese and -rhenium Ethane-1,2-dionyl Compounds

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The synthesis, spectroscopic properties, and reactivity of binuclear manganese and rhenium compounds in which the metals are linked by an ethane-1,2-dionyl bridge are described. The compounds $M(CO)_5C(=O)C(=O)M(CO)_5$ (M = Mn, Re) are prepared by treatment of the respective pentacarbonyl anions with oxalyl chloride. These complexes have been characterized by ^{13}C NMR, IR, UV/visible, and mass spectrometries and, in the case of M = Re, by an X-ray diffraction study. $Re(CO)_5C(=O)C(=O)Re(CO)_5$ crystallizes in space group $P2_1/c$ and has unit cell dimensions $a = 5.627$ (4) Å, $b = 12.392$ (6) Å, $c = 10.192$ (6) Å, and $\beta = 95.69$ (8)° with $Z = 2$. Molecules of the complex lie such that the midpoint of the central C–C bond coincides with a crystallographic inversion center. The central Re–CO–CO–Re unit is planar, with the $Re(CO)_5$ substituents mutually trans and staggered relative to the ethane-1,2-dionyl plane. The dionyl C–Re bonds are of length appropriate to Re–C_{sp^2} single bonds, 2.228 (12) Å, and the central C–C bond is also single, length 1.558 (21) Å. Attempts to convert the ethane-1,2-dionyl moiety, which can be regarded as two carbon–carbon coupled CO molecules, into C_2 oxygenates have not met with much success, either in catalytic or in stoichiometric reactions. Decomposition of the $M_2(CO)_{12}$ species to $M_2(CO)_{10}$ + 2CO (M = Mn, Re) is the preferred reaction in all cases. Aspects of the reactivity of $M(CO)_5C(=O)C(=O)M(CO)_5$ (M = Mn, Re) toward hydride donor reagents, hydrogen, and neopentyllithium are reported.

Introduction

From an industrial point of view, selectivity in conversion of syngas to C_2 products remains a major objective and is therefore a subject of much research.

To date the most generally accepted mechanism in CO hydrogenation involves the initial reduction of a coordinated CO ligand followed by CO insertion, subsequent reduction, and product formation via hydrogenation.[1,2] Mechanisms and examples of reactions involving carbon–carbon bond formation between two CO molecules as a first step and hydrogenation as a second step are much less common despite the fact that, in terms of prospects for C_2 selectivity, this approach looks promising.

An obvious structure resulting from a CO-to-CO coupling would be a compound with an ethane-1,2-dionyl bridge, e.g., $L_nMC(=O)C(=O)ML_n$. In organotransition-metal chemistry neither such compounds nor reactions leading to them are known, although speculations about their possible existence and relevance in catalysis have been put forward by Wilkinson et al.[3]

Examples that bear an important resemblance are the coupling of CO ligands by low valency zirconium compounds reported by Bercaw et al.,[4] the reductive coupling of isocyanide ligands in molybdenum and tungsten complexes reported by Lippard et al.,[5] and, possibly, the coupling of CO ligands in highly reduced metal carbonyls.[6]

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