Contribution from the Department of Chemistry,
University of Houston, Houston, Texas 77004

# Crystal and Molecular Structure and Absolute Configuration of (−)$_{436}$-(η^6-C$_6$H$_6$)Ru(SnCl$_3$)(CH$_3$)[Ph$_2$PNHCH(CH$_3$)Ph]

JAMES D. KORP and IVAN BERNAL*

The X-ray crystal structure of the optically active ruthenium–arene complex (η^6-C$_6$H$_6$)Ru(SnCl$_3$)(CH$_3$)[Ph$_2$PNHCH(CH$_3$)Ph] has been determined in order to correlate the observed chirality with the CD spectrum. It is found that the diastereoisomer that rotates (−) at 436 nm has the *R* configuration, with the assumption of ligand ranking order C$_6$H$_6$ > Sn > P > Me. The phosphine ligand has an additional chiral center, which is also *R*. Crystals are orthorhombic, space group *P*2$_1$2$_1$2$_1$, with four molecules in a unit cell of dimensions *a* = 10.080, *b* = 11.916, and *c* = 24. 301 Å. With use of automatic diffractometer data the final *R* value is 2.9%. The *polyhapto*benzene ring is disordered over two positions 60%:40% (eclipsed:staggered) with respect to the other three ligands of Ru. The coordination about Ru is octahedral, with three facial points collapsed to bond to benzene. Both the trichlorotin and the phosphine ligand exhibit significant distortions from tetrahedral geometry about the central atom as a consequence of bonding to the ruthenium. Pertinent bond lengths are as follows: Ru–Sn = 2.543, Ru–P = 2.295, Ru–Me = 2.155, P–N = 1.653 Å. The average Ru–C(benz) distances are 2.264 and 2.212 Å for the eclipsed and staggered orientations, respectively. There is an intramolecular hydrogen bond from NH to Cl having an N···Cl separation of 3.545 Å and an angle at the hydrogen of 178°.

Introduction

The compound (η^6-C$_6$H$_6$)RuCl(CH$_3$)[Ph$_2$PNHCH(CH$_3$)-Ph] was originally prepared as the first example of an optically active Ru–arene complex.[1] Although both diastereoisomers have stable configurations at room temperature, which are easily separated by dry-column chromatography, suitable single crystals for X-ray studies have so far been unobtainable. Thus it has not been possible to correlate the observed absolute configurations with their respective CD spectra in order to determine the correct chirality at Ru for the more soluble and less soluble isomers. In an attempt to resolve this problem, the analogous SnCl$_3$ derivatives were prepared from the parent Cl compounds via SnCl$_2$ insertion, yielding mixtures of **1a** and **1b**, which were easily separated.[2] Note that only the chirality

1a   **1b**
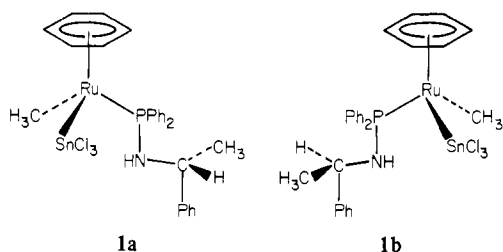
at the metal need be different, not the chirality at the optically active carbon in the phosphine ligand. Since **1b** was the favored product, we obtained single crystals of it and herein report the structural details and spectral correlations. Unfortunately there is still ambiguity with respect to the correct absolute configuration of the Cl parent compound, since the exact nature of the tin species involved in the insertion is not known,[2] and it is not certain whether the reaction occurs with retention or inversion of configuration. Although we had hoped to resolve this question by comparison of CD spectra, it was found that the Cl and SnCl$_3$ compounds give such completely different CD curves that no meaningful conclusions can be reached from them alone.

Two other minor points, which we wished to investigate, were the nature of the Ru–arene conformation and the configuration of the SnCl$_3$ ligand. Several recent papers[3-5] have

Table I. Summary of Data Collection and Processing Parameters

space group	*P*2$_1$2$_1$2$_1$, orthorhombic
cell const	*a* = 10.080 (5) Å, *b* = 11.916 (4) Å, *c* = 24.301 (7) Å, *V* = 2919 Å^3
molecular formula	RuSnCl$_3$PNC$_{27}$H$_{29}$
mol wt	724.63
molecules per cell	*Z* = 4
density	ρ = 1.65 g cm^{-3}
abs coeff	μ = 15.8 cm^{-1}
radiation (Mo Kα)	λ = 0.710 73 Å
collection range	4° ≤ 2θ ≤ 60°
scan width	$\Delta\theta$ = (0.95 + 0.35 tan θ)°
max scan time	120 s
scan speed range	0.7–6.7° min^{-1}
total data collected	4726
indep data with *I* > 3σ(*I*)	1590
total variables	155
$R = \Sigma \|\|F_o\| - \|F_c\|\|/\Sigma \|F_o\|$	0.029
$R_w = [\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.027
weights	$w = (\sigma(F))^{-2}$

looked into the rotational barriers in polyene–ML$_3$ complexes, with both eclipsed[6,7] and staggered[7] Ru compounds being reported. We were curious to see if the bulk of the ligands in our case would force a preferential conformation. It has also been noted that SnCl$_3$ ligands attached to large transition metals exhibit distortions from tetrahedral geometry,[8] and we wished to look into this matter as well.

Experimental Section

The synthesis and isolation of the title compound are reported elsewhere.[2] The crystal used for data collection was an amber-colored columnar prism of approximate dimensions 0.20 × 0.20 × 0.45 mm. All measurements were made on an Enraf-Nonius automatic diffractometer with Mo Kα radiation monochromatized by a dense graphite crystal, assumed for all purposes to be ideally imperfect. Lattice constants and an orientation matrix were obtained from a least-squares fit of 25 centered reflections. Final cell constants as well as other information concerning data collection and refinement are listed in Table I. The Laue symmetry was determined to be *mmm*, and from the systematic absences noted the space group was shown unambiguously to be the noncentrosymmetric *P*2$_1$2$_1$2$_1$. This is consistent with the knowledge that the molecule is chiral. Intensity data were collected with use of the θ–2θ scan technique, with two standard reflections being monitored after every 2 h of X-ray exposure time to check crystal stability. During the course of the data collection,

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Table II. Atomic Coordinates and Thermal Parameters ($\times 1000$; Ru and Sn $\times$ 10 000)

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ru	0.10302 (10)	0.52535 (8)	0.48062 (4)	399 (6)	344 (5)	370 (6)	−32 (6)	27 (6)	−20 (5)
Sn	0.12256 (10)	0.32895 (7)	0.44048 (4)	630 (6)	320 (4)	577 (6)	116 (6)	−9 (7)	3 (5)
Cl1	0.1533 (5)	0.1815 (3)	0.5044 (2)	165 (5)	55 (2)	80 (3)	30 (3)	−4 (3)	21 (2)
Cl2	0.3023 (4)	0.2844 (3)	0.3805 (2)	118 (4)	68 (3)	96 (3)	43 (3)	44 (3)	4 (3)
Cl3	−0.0439 (4)	0.2380 (3)	0.3883 (2)	118 (4)	54 (3)	137 (4)	4 (3)	−48 (3)	−25 (3)
P	0.0530 (3)	0.5970 (3)	0.3954 (1)	33 (3)	30 (2)	42 (2)	−2 (2)	3 (2)	−1 (2)
N	0.1215 (10)	0.5282 (8)	0.3436 (4)	42 (6)	39 (6)	48 (6)	12 (7)	1 (6)	−10 (6)
C1	0.3046 (9)	0.5518 (11)	0.4540 (5)	31 (7)	104 (11)	29 (8)	−12 (8)	2 (6)	3 (8)
C20	0.0962 (13)	0.5515 (11)	0.2838 (5)	36 (8)	64 (9)	45 (8)	−4 (9)	−8 (8)	−9 (7)

atom	x/a	y/b	z/c	U, Å²	atom	x/a	y/b	z/c	U, Å²
C2	0.1346 (22)	0.4863 (21)	0.5703 (8)	54 (2)	H1B	0.3456 (9)	0.6342 (11)	0.4613 (5)	90 (23)
C3	0.0121 (22)	0.4420 (21)	0.5548 (8)	54 (2)	H1C	0.3335 (9)	0.5232 (11)	0.4136 (5)	90 (23)
C4	−0.0843 (22)	0.5117 (21)	0.5318 (8)	54 (2)	H2	0.2037 (22)	0.4363 (21)	0.5868 (8)	100 (0)
C5	−0.0581 (22)	0.6256 (21)	0.5243 (8)	54 (2)	H3	−0.0067 (22)	0.3604 (21)	0.5602 (8)	100 (0)
C6	0.0645 (22)	0.6699 (21)	0.5397 (8)	54 (2)	H4	−0.1722 (22)	0.4300 (21)	0.5207 (8)	100 (0)
C7	0.1608 (22)	0.6002 (21)	0.5627 (8)	54 (2)	H5	−0.1272 (22)	0.6756 (21)	0.5077 (8)	100 (0)
C2′	0.0937 (41)	0.4493 (20)	0.5636 (14)	54 (2)	H6	0.0833 (22)	0.7515 (21)	0.5343 (8)	100 (0)
C3′	−0.0353 (41)	0.4617 (20)	0.5438 (14)	54 (2)	H7	0.2487 (22)	0.6319 (21)	0.5739 (8)	100 (0)
C4′	−0.0797 (41)	0.5667 (20)	0.5263 (14)	54 (2)	H2′	0.1255 (41)	0.3741 (20)	0.5762 (14)	100 (0)
C5′	0.0048 (41)	0.6592 (20)	0.5286 (14)	54 (2)	H3′	−0.0959 (41)	0.3954 (20)	0.5421 (14)	100 (0)
C6′	0.1338 (41)	0.6468 (20)	0.5485 (14)	54 (2)	H4′	−0.1722 (41)	0.5756 (20)	0.5120 (14)	100 (0)
C7′	0.1783 (41)	0.5419 (20)	0.5660 (14)	54 (2)	H5′	−0.0271 (41)	0.7345 (20)	0.5161 (14)	100 (0)
C8	−0.1246 (6)	0.6059 (6)	0.3773 (3)	39 (3)	H6′	0.1944 (41)	0.7132 (20)	0.5502 (14)	100 (0)
C9	−0.2096 (6)	0.5224 (6)	0.3967 (3)	55 (4)	H7′	0.2707 (41)	0.5330 (20)	0.5802 (14)	100 (0)
C10	−0.3434 (6)	0.5235 (6)	0.3820 (3)	61 (4)	H9	−0.1746 (6)	0.4619 (6)	0.4213 (3)	100 (0)
C11	−0.3922 (6)	0.6080 (6)	0.3479 (3)	78 (4)	H10	−0.4043 (6)	0.4637 (6)	0.3960 (3)	100 (0)
C12	−0.3072 (6)	0.6914 (6)	0.3284 (3)	64 (4)	H11	−0.4881 (6)	0.6088 (6)	0.3373 (3)	100 (0)
C13	−0.1734 (6)	0.6903 (6)	0.3431 (3)	58 (4)	H12	−0.3422 (6)	0.7520 (6)	0.3038 (3)	100 (0)
C14	0.1052 (8)	0.7424 (4)	0.3887 (3)	37 (3)	H13	−0.1125 (6)	0.7502 (6)	0.3291 (3)	100 (0)
C15	0.0336 (8)	0.8268 (4)	0.4152 (3)	56 (4)	H15	−0.0449 (8)	0.8070 (4)	0.4384 (3)	100 (0)
C16	0.0715 (8)	0.9387 (4)	0.4093 (3)	63 (4)	H16	0.0202 (8)	0.9992 (4)	0.4283 (3)	100 (0)
C17	0.1810 (8)	0.9663 (4)	0.3769 (3)	61 (4)	H17	0.2082 (8)	1.0466 (4)	0.3727 (3)	100 (0)
C18	0.2526 (8)	0.8820 (4)	0.3504 (3)	67 (4)	H18	0.3311 (8)	0.9018 (4)	0.3272 (3)	100 (0)
C19	0.2147 (8)	0.7700 (4)	0.3563 (3)	43 (3)	H19	0.2660 (8)	0.7096 (4)	0.3373 (3)	100 (0)
C21	0.0184 (16)	0.4556 (14)	0.2599 (7)	102 (6)	H20	0.0415 (87)	0.6337 (72)	0.2791 (34)	34 (31)
C22	0.2261 (7)	0.5653 (8)	0.2541 (3)	50 (4)	H21A	0.0610 (16)	0.3748 (14)	0.2501 (7)	100 (0)
C23	0.3236 (7)	0.4825 (8)	0.2575 (3)	73 (5)	H21B	0.0029 (16)	0.5024 (14)	0.2224 (7)	100 (0)
C24	0.4456 (7)	0.4981 (8)	0.2315 (3)	92 (6)	H21C	−0.0754 (16)	0.4437 (14)	0.2806 (7)	100 (0)
C25	0.4701 (7)	0.5965 (8)	0.2021 (3)	82 (5)	H23	0.3061 (7)	0.4120 (8)	0.2786 (3)	100 (0)
C26	0.3726 (7)	0.6793 (8)	0.1986 (3)	100 (5)	H24	0.5155 (7)	0.4388 (8)	0.2339 (3)	100 (0)
C27	0.2506 (7)	0.6637 (8)	0.2247 (3)	84 (5)	H25	0.5575 (7)	0.6077 (8)	0.1834 (3)	100 (0)
H(N)	0.1784 (86)	0.4469 (71)	0.3560 (37)	44 (33)	H26	0.3901 (7)	0.7498 (8)	0.1776 (3)	100 (0)
H1A	0.3414 (9)	0.4941 (11)	0.4846 (5)	90 (23)	H27	0.1806 (7)	0.7230 (8)	0.2222 (3)	100 (0)

these standards varied by less than 3% of their original intensity. In the reduction of the data, Lorentz and polarization factors were applied, but no correction was made for absorption.

The structure was solved via MULTAN,[9] which yielded the correct positions of the Ru, Sn, P, and Cl atoms. The Patterson map was quite confusing due to the large number of heavy atoms and the piling up of many of the interatomic vectors. Difference Fourier syntheses revealed all the remaining nonhydrogen atoms, although the benzene ring was badly misshapen. Due to the large number of atoms involved, and since there was no reason to expect any meaningful deformations of the three phenyl rings, they were all refined as rigid bodies with hydrogens riding at a fixed distance of 1.0 Å. And since the benzene ring was so poorly located, it too was entered ideally as a rigid body with a fixed temperature factor, at which point the shadow of a companion ring appeared in an almost perfectly staggered position. When the two rings were refined as rigid bodies and constrained to have identical thermal parameters, the population factors converged at 60% for the eclipsed form (with respect to the Ru–P–Sn–C moiety) and 40% for the staggered form. The two methyl groups were also refined as rigid bodies since the individual hydrogens could not all be located. The correct absolute configuration was determined from the analysis of nine Bijvoet pairs[10] of high-intensity reflections, each of which specified the same handedness. After all shift:esd ratios were less than 0.2, convergence was reached at the agreement factors listed in Table I. Final positional and thermal parameters are presented

Table III. Intramolecular Bond Distances (Å)[a]

Ru–Sn	2.543 (1)	Ru–C6′	2.216 (39)
Ru–P	2.295 (3)	Ru–C7′	2.218 (38)
Ru–C1	2.155 (9)	Sn–Cl1	2.366 (3)
Ru–C2	2.251 (18)	Sn–Cl2	2.385 (4)
Ru–C3	2.253 (24)	Sn–Cl3	2.366 (4)
Ru–C4	2.266 (24)	P–N	1.653 (9)
Ru–C5	2.278 (17)	P–C8	1.847 (6)
Ru–C6	2.276 (23)	P–C14	1.819 (6)
Ru–C7	2.262 (23)	N–C20	1.502 (13)
Ru–C2′	2.213 (27)	N–H(N)	1.17 (8)
Ru–C3′	2.208 (34)	C20–C21	1.50 (2)
Ru–C4′	2.206 (34)	C20–C22	1.51 (1)
Ru–C5′	2.211 (27)	C20–H20	1.13 (8)

[a] All distances not shown were idealized as follows: C–C = 1.395, C–H(Me) = 1.08, C–H(aromatic) = 1.00 Å.

in Table II, according to the atom labeling scheme of Figure 1. The atomic scattering factors for the nonhydrogen atoms were computed from numerical Hartree–Fock wave functions;[11] for hydrogen those of Stewart, Davidson, and Simpson[12] were used. The anomalous dispersion coefficients of Cromer and Liberman[13] were used for Ru, Sn, Cl, and P. All calculations were made with the SHELX-76 series of programs.[14] The only high correlations noted between variables

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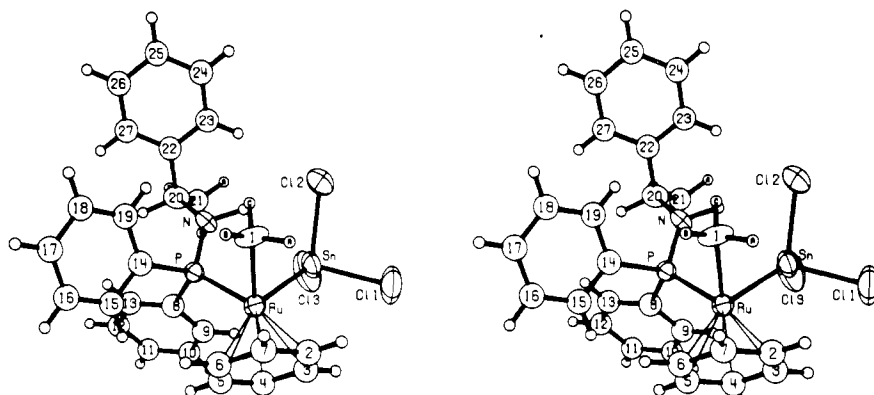
Figure 1. Stereoscopic view of the molecule with the atom labeling scheme. Hydrogens are numbered the same as the carbon to which each is attached. The heavy atoms are shown as 50% equiprobability envelopes with hydrogens as spheres of arbitrary diameter. Only one orientation of the disordered *polyhapto*benzene is shown.

Table IV. Intramolecular Bond Angles (Deg)[a]

Sn-Ru-P	90.8 (1)	Ru-P-N	114.3 (4)
Sn-Ru-Cl	86.9 (4)	Ru-P-C8	116.7 (3)
P-Ru-Cl	83.2 (3)	Ru-P-C14	111.9 (3)
Cent-Ru-Sn	124.4 (8)	N-P-C8	104.5 (4)
Cent-Ru-P	131.5 (8)	N-P-C14	106.4 (5)
Cent-Ru-Cl	126.0 (8)	C8-P-C14	101.8 (4)
Cent'-Ru-Sn	124.4 (8)	P-N-C20	125.1 (8)
Cent'-Ru-P	133.8 (10)	P-N-H(N)	115 (5)
Cent'-Ru-Cl	123.1 (13)	C20-N-H(N)	119 (5)
Ru-Sn-Cl1	116.2 (1)	N-C20-C21	108.8 (11)
Ru-Sn-Cl2	119.9 (1)	N-C20-C22	109.7 (10)
Ru-Sn-Cl3	124.9 (1)	N-C20-H20	110 (4)
Cl1-Sn-Cl2	97.8 (1)	C21-C20-C22	110.5 (11)
Cl1-Sn-Cl3	96.0 (2)	C21-C20-H20	112 (5)
Cl2-Sn-Cl3	96.3 (2)	C22-C20-H20	106 (5)

[a] Cent and Cent' denote the geometric centers of the C2-C7 and C2'-C7' benzene rings, respectively. The phenyl rings have idealized angles of 120° and the methyl groups angles of 109.5°.

occurred within the rigid groups and, as expected, between parameters of the disordered benzene rings. Intramolecular bond lengths and angles are presented in Tables III and IV, and least-squares planes and torsion angles are presented in Tables V and VI in the supplementary material. Tables III–VI are based on the positions of Table II.

Results and Discussion

As can be seen in Figure 1, the molecule consists of a central Ru atom, with four ligands forming a "piano stool" arrangement about it. Although the coordination about Ru might appear to be a distorted tetrahedron, it is probably more accurate to refer to it as an octahedron with three facial points collapsed to form the bond to the *polyhapto*benzene. The three angles associated with P, Cl, and Sn range from 83 to 91°, with the smaller two possibly reflecting some steric repulsion between the methyl group and the benzene. Such an octahedral arrangement is commonly found in related compounds,[7,15-17] along with the slight angular compression in some cases.[7,16] The Ru is a chiral center, along with C20 in the phosphine ligand. With use of the extension of the *R,S* system[18] for *polyhapto* ligands in organometallic compounds,[19] and with the assumption $C_6H_6 > Sn > P > Me$, the configuration at the Ru is seen to be *R*, and this corresponds to the

isomer that rotates (−)436 in the CD spectrum. If the sum of atomic numbers rule[18] is invoked to decide between the relative ranking of Sn and C_6H_6, the Sn ligand outranks C_6H_6 and thus the configuration at Ru should be described as *S*. The handedness of C20 is *R*, which is in accord with the fact that (*R*)-(+)-Ph2PNHCH(CH3)Ph was used in the original synthesis.[1,2] The $SnCl_2$ insertion would have had no effect on this ligand, and so it provides a good internal confirmation of the independent Bijvoet measurements (vide supra).

As stated in the Experimental Section, the benzene ring occupies two positions, staggered and somewhat skewed to each other (see Table V, supplementary material). Only the major component (60%) is shown in Figure 1, and it is in the eclipsed form with respect to the other three ligands. Although it is unusual to find both the eclipsed and staggered forms in the same crystal structure, it is by no means unique.[20] The average Ru–C distances are 2.264 (C2–C7) and 2.212 Å (C2'–C7'), and the Ru to ring centroid distances are 1.785 (Cent) and 1.716 Å (Cent'). Both sets of figures show the staggered ring to be closer to the Ru than the eclipsed one, an observation which might be construed to support a sterically favored conformation. Many examples of both staggered[5,7,16,21,22] and eclipsed[6,23-26] arrangements are known involving several transition metals, and so the steric preference must be very slight indeed. Ru–Cent distances of 1.67–1.79 Å are reported,[16,20,27,28] with the shorter ones belonging to the staggered systems, as in our case. Recent research by Albright et al.[3,4] on the basis of MO calculations shows that the energy difference between the eclipsed and staggered forms (for unsubstituted benzene) should be quite small, which the present investigation indicates.

The trichlorotin ligand shows the same angular distortions found in previous determinations reported in Pd,[29] Ir,[8,30] Fe,[31] and Mn[32] compounds, as well as in the SnBr3 analogue.[33] In

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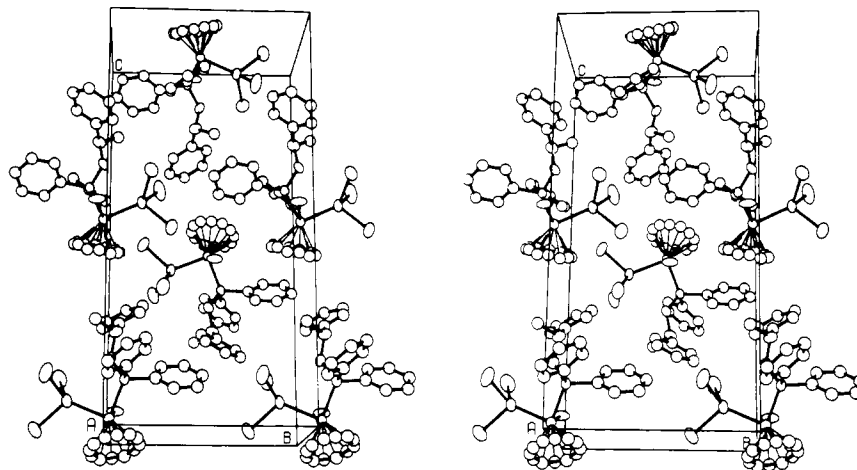
Figure 2. Stereoscopic view of the molecular packing in the unit cell, as viewed into the *a* axis, with the hydrogens omitted for clarity. Both positions of the disordered benzene are shown simultaneously, and in the upper right molecule it can be clearly seen that the ring in the staggered orientation is slightly closer than the eclipsed one.

all of these cases, the M–Sn–X angles are substantially greater and the X–Sn–X angles substantially less than the ideal tetrahedral value of 109.5°. Similar patterns are found in the Ge[6] and Si[34] trihalides, and to a much lesser degree in the SnR$_3$ complexes.[35–39] The reason for the distortion is not steric compression but is instead a consequence of the state of hybridization of the tin atom.[31] According to Fenton and Zuckerman, in a paper on the nature of the tin–transition-metal bond, there is enhanced s character in the Ru–Sn bond from the tin 5s orbital, and this tends to shorten the bond and enlarge the Ru–Sn–Cl angles.[40] A similar theory appeared earlier by Bent.[41] The amount of shortening of the bond seems to vary directly with the electron-withdrawing power of the substitutents on tin, making Fe–SnPh$_3$ longer than Fe–SnCl$_3$ for example.[31] Our bond length for Ru–Sn of 2.543 (1) Å is in fact seen to be significantly shorter than the values [2.691 (1) and 2.673 (3) Å] found in two Ru–SnMe$_3$ complexes,[35,38] and as mentioned above, these compounds also exhibit much smaller angular distortions. More s character in the Ru–Sn bond implies more p character in the Sn–Cl bonds, but since thermal libration tends to abnormally shorten them, this effect is more difficult to verify. Our values average 2.372 Å, which is in good agreement with results reported for other trichlorotin ligands.[8,29,31,42]

There is a paucity of information in the literature concerning methyl–ruthenium bonding. Our Ru–C1 distance of 2.16 Å is 0.04 Å shorter than that observed in Ir–CH$_3$,[43] which is very close to the difference in covalent radii between Ru and Ir.[44] It is considerably larger, however, than the Ru–C distances reported in a trimethylene-bridged Ru$_2$ complex,[45] although this may be due to slightly different orbital hybridizations. As mentioned above, the methyl group shows the furthest distortion from orthogonality with the other ligands and is possibly experiencing a slight steric repulsion from the benzene. Figure 1 shows that the hydrogens are staggered with respect to the Ru–P and Ru–Sn bonds, and apparently to the benzene hydrogens as well. But it should be remembered that only one of the two benzene configurations is shown, and in fact the other, which eclipses the methyl hydrogens, is actually closer to the ruthenium.

The remaining ligand, an optically active tertiary phosphine, was used in the original synthesis of the parent chloro derivative as a resolving agent to produce a pair of diastereoisomers, which could be easily separated chromatographically.[1] Although the phenyls were treated as rigid bodies, the P–C bonds (average 1.83 Å) refined to values well within the range reported in the literature.[7,30,32,46,47] The P–N value of 1.65 Å is somewhat long comparatively although in good agreement with the average of 1.66 Å in tetrametaphosphimic acid, wherein the NH plays a similar role.[48] The observed C–N distance of 1.50 Å is exceedingly long, being at the upper limit of reported values, and comparable only to those distances observed in compounds such as (CH$_3$NH$_3$)$_2$MnCl$_4$.[49] We have recently reported the X-ray crystal structure of an iron complex with the *S* isomer of this same ligand, and we find that all the homologous bonds are essentially equal in length with the sole exception of the C–N bond, which is only 1.47 Å in that structure.[50]

The Ru–P distance of 2.295 (3) Å is somewhat shorter than the literature average (2.35 Å, range 2.32–2.42 Å),[7,27,45,46,51] which could indicate a slightly stronger than usual bonding. As in the case of the SnCl$_3$ ligand, the angles about the phosphorus atom are significantly distorted from tetrahedral, with the Ru–P–C(N) average being 114.3° and the C–P–C(N) average 104.2°. Some of the other phosphine–transition-metal complexes in the literature show greater distortions,[30,47] and some show less.[29,32] The divergence of reported values has been attributed to variations in the amount of π bonding between the metal and the phosphorus atoms, similar to the M–Sn case mentioned previously. There may be some perturbation in the present structure, however, since the nitrogen participates in an intramolecular hydrogen bond to one of the chlorines, as can be seen in Figure 1. The pertinent values are N$\cdots$Cl2 =

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3.545 Å and angle N-H···Cl2 = 178°, and these values compare favorably with previously reported NH to Cl hydrogen bonds.[49,52,53] The severely acute H···Cl-Sn angle (65°) is not unusual when halides are involved, for example, in the case of Co(en)$_3$[3+] where a chloride ion is hydrogen bonded to three of the ethylenediamine nitrogens of a trigonal face.[53]

The packing of the molecules is shown in Figure 2, in which it can be seen that there are no unusually close intermolecular contacts. The highly electronegative chlorine groups are quite well segregated from one another, as the molecules align themselves in chains parallel to the *b* axis. The perfectly staggered orientations of the disordered benzene ring are also shown.

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Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

Dealkylation and Reductive Coupling of *tert*-Butyl Isocyanide Ligands in Heptakis(*tert*-butyl isocyanide)molybdenum(II). Structure of Seven-Coordinate Cyanotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)acetylene)molybdenum(II) Tetraphenylborate[1,2]

JOHN C. DEWAN, CHRISTEN M. GIANDOMENICO, and STEPHEN J. LIPPARD*

The reaction of heptacoordinate [Mo(CN-*t*-Bu)$_7$][2+] with zinc in refluxing ethanol produces the [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)(CN)][+] cation in 27% yield. This new complex contains the coupled ligand product (*N*,*N'*-di-*tert*-butyldiamino)acetylene and coordinated cyanide ion that arises from dealkylation of *tert*-butyl isocyanide. An X-ray crystallographic study of the tetraphenylborate salt of cyanotetrakis(*tert*-butyl isocyanide)((*N*,*N'*-di-*tert*-butyldiamino)-acetylene)molybdenum(II) has been carried out. The compound crystallizes in the orthorhombic space group *Pccn* with Z = 4. The unit cell dimensions are *a* = 16.349 (3) Å, *b* = 19.724 (3) Å, and *c* = 17.752 (4) Å. The molybdenum and cyanide C and N atoms lie on a crystallographically required twofold axis that passes through the midpoint of the acetylenic C–C bond. Unlike other [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)X][+] cations, where X = Br or I, the present structure more closely resembles pentagonal-bipyramidal rather than capped trigonal-prismatic idealized geometry. The two axial *tert*-butyl isocyanide ligands have Mo–C bond lengths of 2.121 (5) Å, and the corresponding C–Mo–C angle is 175.7 (3)°. The equatorial Mo–C bond lengths are 2.204 (6) Å for the cyanide ion, 2.143 (5) Å for the *tert*-butyl isocyanide groups, and 2.053 (4) Å for the bidentate coupled ligand. Other features of the coupled ligand geometry include a rather long acetylenic C–C bond of 1.402 (8) Å, C–N bond distances of 1.312 (5) and 1.472 (6) Å for the alkynyl and alkyl fragments, respectively, and respective C–C–N and C–N–C angles of 127.9 (3) and 128.5 (4)°. The HNCCNH unit is planar to within ±0.04 Å. Distortions of the cation are discussed in terms of hydrogen bonding and intramolecular steric interactions. Its molecular geometry and those of the other [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)X][+] cations are analyzed according to Kepert's ligand–ligand repulsion model for seven-coordinate stereochemistries.

Introduction

The reaction of the seven-coordinate [Mo(CN-*t*-Bu)$_6$X][+] cations, X = Cl, Br, I, CN, with zinc in tetrahydrofuran produces [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)X][+] complexes in which two adjacent ligands have reductively coupled to form the coordinated (*N*,*N'*-di-*tert*-butyldiamino)acetylene molecule.[3,4] An attempt was made to extend this chemistry to the parent cation,[5] [Mo(CN-*t*-Bu)$_7$][2+]. Surprisingly, the product was found to be [Mo(CN-*t*-Bu)$_4$(*t*-BuHNCCNH-*t*-Bu)(CN)][+], in which not only reductive coupling but also dealkylation of one of the *tert*-butyl isocyanide ligands had occurred. The latter reaction, which has been independently verified in thermal decomposition studies of [M(CN-*t*-Bu)$_7$][2+] (M = Mo, W) cations,[6] serves as a striking illustration of the propensity of metal-coordinated isocyanides, especially *tert*-butyl derivatives, to lose carbonium ions with concomitant formation of the metal–cyanide linkage.[7] Here we describe the synthesis and the crystal and molecular structure of the new complex, isolated as the tetraphenylborate salt. The results also contribute to the current information pool on the stereochemistry of seven-coordinate transition-metal complexes, a subject of considerable theoretical interest.[8,9] The

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