matography on Florisil. Conversion of enol ether **8** into the sodium salt **9**, considered to be the biological equivalent of prostacyclin,[5] was accomplished by saponification with 1 equiv of sodium hydroxide in methanol-water (1:1). Following lyophilization, **9** (100% yield) was obtained as a hygroscopic, free flowing white powder; IR (ν, mull) 3320 (OH),1693 (-O-C=C), 1555, 1470, cm^{-1} (CO_2-); stable for at least two months if kept dry at −30 °C.

To determine the stereochemistry of the C_5–C_6 double bond in prostacyclin, the double-bond isomer of enol ether **8** was prepared and the NMR spectra of the two isomers were compared. We reasoned that, if the reactions giving iodo ether **3a** and enol ether **8** are stereospecific as shown in Scheme I (i.e., trans addition and trans elimination), then application of this reaction sequence to 5-*trans*-$PGF_{2\alpha}$ methyl ester should give the isomeric enol ether. Accordingly, reaction of 5-*trans*-$PGF_{2\alpha}$ methyl ester[16] (0.005 mol) with iodine (0.005 mol) and sodium carbonate (0.010 mol) in CH_2Cl_2 (35 ml) gave a major iodo ether (**10a**, 0.0019 mol, mass spectrum of bis(trimethylsilyl) derivative calcd 638.2321, found 638.2333), a minor iodo ether (**10b**. 0.00033 mol, *m/e* calcd 638.2321, found 638.2327, and recovered starting material (0.0018 mol) following workup and chromatographic separation. Dehydroiodination of the major iodo ether (**10a**, 0.0035 mol) with excess KO_2 in DMF gave only isomeric enol ether **11** (0.00082 mol): mp 68-70 °C; ^1H NMR ($CDCl_3$, δ) 5.53 (m, 2 H, -CH=CH-), 4.67 (m, 1 H, -O-C=CH-), 4.52 (m, 1 H, >CH-O), 4.02 (m, 1 H, $-HC_{15}$-O-), 3.82 (m, 1 H, >CH-O), 3.67 (s, 3 H, $-OCH_3$), 0.88 (t, 3 H, J = 5 Hz, $-CH_3$); ^{13}C NMR ($CDCl_3$, ppm from Me_4Si) 174.3 (C_1), 155.9 (C_6), 136.4 (C_{14}), 131.3 (C_{13}), 95.9 (C_5), 83.0 (C_9), 77.3 (C_{11}), 72.9 (C_{15}), 55.5 (C_{12}), 51.4 (C_{21}), 45.6 (C_8), 40.4 (C_{10}), 37.2 (C_{16}), 33.4 (C_2), 31.7 (C_{18}), 30.5 (C_7), 26.9 (C_4), 25.7 (C_3), 25.2 (C_{17}), 22.6 (C_{19}), 14.0 (C_{20}); IR (ν, liquid melt) 3420 (OH), 1740 (C=O), 1690 cm^{-1} (-O-C=C); TLC (silica gel,[14] 1:1 acetone–hexane) R_f 0.65. Hydrolysis of **11** with aqueous pH 2 buffer in tetrahydrofuran (1:1)[5] gave 6-keto-$PGF_{1\alpha}$ methyl ester. Saponification of **11**, as described above for **8**, gave the sodium salt **12**.

Scheme I predicts that **8** and **11** will have the configurations of 5Z and 5E, respectively. Perusal of the NMR data for enol ethers reveals that the signals for the vinyl protons cis to the ether oxygen invariably are downfield from those for the isomeric trans protons.[17] Consequently, the finding of signals for the C_5 protons at δ 4.16 in **8** and at 4.67 in **11** confirms the assignment of the 5Z configuration to enol ether **8** and thereby to prostacyclin.

Finally, we note that enzymatically prepared prostacyclin methyl ester containing radiolabel[5] cochromatographs with **8** when a mixture of **8** and **11** is placed on a silica gel TLC plate and developed in 1:1 acetone–hexane.

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(12) The stereochemistry shown for structure **3a**, (5R,6R)-5-iodo-9-deoxy-6,9α-epoxy-$PGF_{1\alpha}$ methyl ester is assigned as a consequence of the assumed stereospecific iodo ether formation and subsequent elimination of HI during the synthesis of compound **8** (see Scheme I). An assignment of 5S,6S would also be compatible with this reaction sequence but would require a much more sterically hindered molecular conformation (easily seen in molecular models) during the reaction forming the iodo ether. The 5S,6S assignment is given to the iodo ether (**3b**) formed in minor yield (2–10%) in this reaction. It may also be expected that the exo configuration, which is pseudoequatorial with regard to the 2-oxabicyclo[3.3.0]octane ring system, will be the thermodynamically favored configuration for compounds that are epimeric at C_6. Similar reasoning is used for the assignment of stereochemistry to **10a**, (5S,6R)-5-iodo-9-deoxy-6,9α-$PGF_{1\alpha}$ methyl ester, and **10b**, (5R,6S)-5-iodo-9-deoxy-6,9α-$PGF_{1\alpha}$ methyl ester. An important feature distinguishing **3a** and **3b** as well as **10a** and **10b** is the presence of a multiplet (an ill-defined quartet, integrating for one proton) at δ 4.55 in the NMR spectra ($CDCl_3$) of **3a** and **10a** and the absence of any signal in this area of the NMR spectra of **3b** and **10b**. A similar contrast is seen in the spectrum of **4** (4.45) and its C_6 epimer (no signal).

(13) We attribute the wide ranging melting points found for **7** and **2** to the hemiketal hydroxy ketone equilibrium expected for 1,4-hydroxy ketones.

(14) The use of silica gel coated plates for thin layer chromatography is successful if the plate is developed immediately after spotting. Column chromatography on silica gel is unsuccessful, however, even if triethylamine is added to the solvent. 6-Keto-$PGF_{1\alpha}$ methyl ester is isolated from such attempted column purifications.

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Received February 18, 1977

Stabilization of One-Dimensional Conducting Materials by Carbonyl Ligands. Crystal and Molecular Structure of $Ir(CO)_3Cl$[1]

Sir:

We wish to report the characterization of $Ir(CO)_3Cl$, a one-dimensional highly conducting stoichiometric material in which chains containing short Ir metal-metal bonds of length 2.844 (1) Å are stabilized without mixed valency or charge transfer to interstitial anions within the lattice.

Recently controversy has arisen concerning the material originally characterized as $Ir(CO)_3Cl$ and later reported to be nonstoichiometric, $Ir(CO)_3Cl_{1.1}$. $Ir(CO)_3Cl$ was first synthesized by Hieber and Lagally[2] and later by Fischer and Brenner,[3] both groups reporting chemical analyses indicating a stoichiometric Cl content. Later Krogmann et al.[4] reported a preliminary x-ray structure of the Ir compound but gave the stoichiometry as $Ir(CO)_{2.93}Cl_{1.07}$ based on an unpublished chemical analysis. Since the structure of this compound involved stacked square planar groups and short Ir-Ir distances, it was described as similar to the partially oxidized cyanoplatinate compounds which share similar physical properties and structures. The reported chemical formulation was rationalized by suggesting that a small amount of $Ir(CO)_2Cl_2$ was incorporated into the crystal. Ginsberg[5] resynthesized this material and reported a chemical analysis consistent with the formulation, $Ir(CO)_3Cl_{1.1}$. He concluded that the excess Cl^- ion must reside interstitially within the crystalline lattice on the basis of Ir^{193} Mössbauer data which suggest Ir is present in a single-valence state and also magnetic susceptibility data which

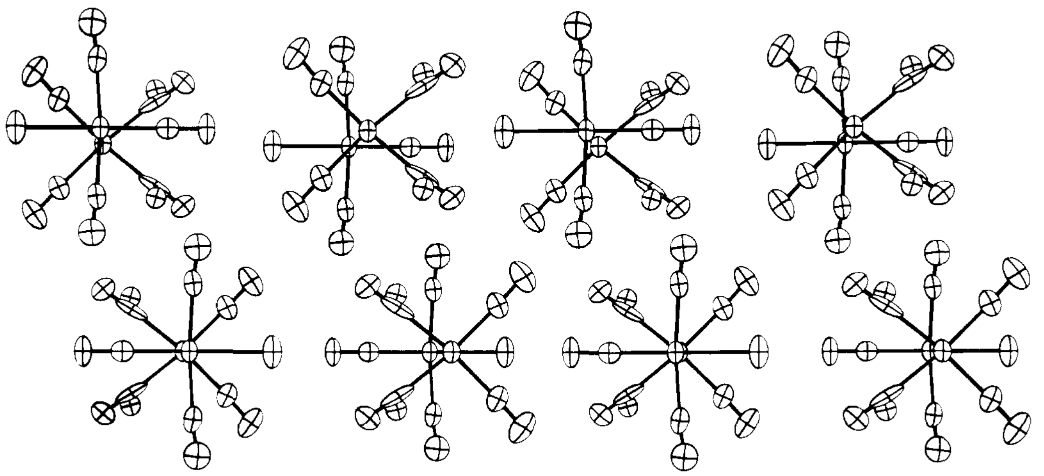

Figure 1. A stereoview of a unit cell of $Ir(CO)_3Cl$ viewed down the *a* axis. The close packing of $Ir(CO)_3Cl$ units is easily observed.

Table I. Elemental Analysis of $Ir(CO)_3Cl$ Sample[a,b]

	% Ir	% C	% Cl
Calcd $Ir(CO)_3Cl_{1.1}$	60.97	11.43	12.37
Calcd $Ir(CO)_3Cl$	61.67	11.56	11.37
Single-crystal Sample,[c] two sublimations in CO	61.92	11.36	10.90
Powder sample, two sublimations in CO	61.98	11.20	11.11

[a] Elemental analysis performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. [b] O_2 cannot be determined in the presence of Ir, C, and Cl. [c] The calculated stoichiometry determined from the single-crystal sample and based on integral CO is $Ir_{1.02}(CO)_3Cl_{0.98}$.

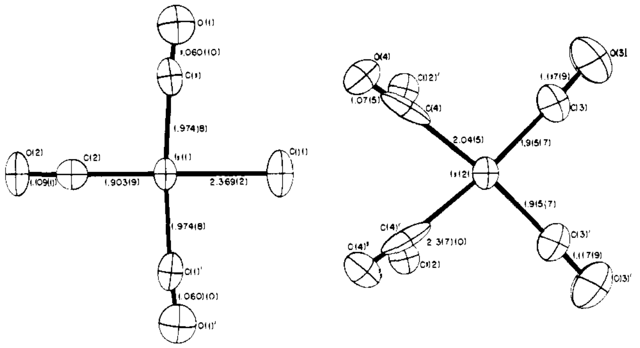

Figure 2. Atom labeling and bond distances within the two different $Ir(CO)_3Cl$ units.

rules out the presence of Ir^{+2}. These results are consistent with those of Dahl[6] who showed no $IrCl_2^+$ fragments in the mass spectra. However, contrary to these results is the observation that this material sublimes readily at 150 °C in a stream of CO,[7] which seems to be inconsistent with an ionic state. A quite different objection to the formulation $Ir(CO)_3Cl_{1.1}$ is that it implies an $Ir^{1.1}$ oxidation state which suggests a very weak Ir–Ir bond of bond number 0.1[8,9] and an expected Ir–Ir bond distance of 3.16 Å. The observed distance, 2.844 Å, corresponds to a stronger bond of bond number ~0.3 and an oxidation state of $Ir^{1.3}$. Thus a much larger amount of Cl^- ion is expected to be present if this material is to be described similarly to the Pt 1-D materials.[4] The class of anionic iridium carbonyl halide complexes, $R_xIr(CO)_2Cl_2$ ($x = 0.38$–0.52) characterized by Krogmann[10] and Ginsberg[11] are cases in point. Therefore since no complete structural analysis of $Ir(CO)_3Cl$ has been reported, we undertook the current study to determine the correct stoichiometry and the nature of the stabilization of this 1-D material.

$Ir(CO)_3Cl$ was prepared by the method of Fischer and Brenner.[3] Two sublimations at 150 °C in a CO stream resulted in long copper-brown fibers or needle crystals which are orthorhombic, space group, C_{mcm} ($D_{2h}{}^{17}$, No. 63), with cell dimensions $a = 5.687$ (2), $b = 15.168$ (5), $c = 12.909$ (7) Å, and $Z = 8$. The chemical analysis of this material is shown in Table 1 along with the calculated values for $Ir(CO)_3Cl_{1.1}$ and $Ir(CO)_3Cl$. Only single x-ray sized crystals were used for one of the determinations in order that the structural and chemical analysis data would be for similar samples. This table clearly indicates that the stoichiometry of our samples is $Ir(CO)_3Cl$, showing no excess halide. Four octants (hkl, $h\bar{k}l$, $hk\bar{l}$, $h\bar{k}\bar{l}$) of three dimensional x-ray data were collected on a Syntex $P2_1$ automatic diffractometer using Mo $K\alpha$ radiation in the θ–2θ scan mode to a 50° 2θ limit. The data was corrected for absorption, averaged over the four octants ($R_{\mathrm{av.\,int.}} = 0.020$), and the structure solved by a combination of Patterson, Fourier, and least-squares refinement techniques. All atoms were refined anisotropically to a final $R_{F^2} = 0.019$ for 501 reflections with no reflections considered unobserved. This very low discrepancy index reflects the high accuracy of our structural model and the completeness of our refinement.

The chief structural findings which relate directly to the one-dimensional character follow. (1) Two crystallographically different Ir atoms at (0, 0.083, ¼) and (0, 0.581, ¼) give a single Ir–Ir bond distance of 2.844 (1) Å and a Ir(1)–Ir(2)–Ir(1) bond angle of 178.53 (2)°. (2) Staggered planar $Ir(CO)_3Cl$ molecules are stacked parallel to the *a* axis (see Figure 1); (3) A stacking disorder of $Ir(2)(CO)_3Cl$ groups results in a close overlap of the Cl and one CO ligand (see Figure 2). The 50% positional disorder was completely resolvable owing to the excellent refinement and each atom was refined anisotropically. Following the normal refinement the multipliers of each of the disordered atoms were included as variables;[12] no change from the 50% weighting initially assumed was found. Figures 1 and 2 show an elongated ellipsoid for the C atom and a normal ellipsoid for the Cl and O atoms involved in the 50% disorder. A large overlap correlation exists between the C and Cl atoms, but is smaller for the O and Cl atoms. In additional trials the multipliers of the disordered atoms were fixed but the C and O atoms were weighted 10% higher and the Cl 10% lower; the C ellipsoid then became quite normal. When the Cl atom was weighted 10% higher as would be for excess $Ir(CO)_2Cl_2$ units along the chain, and the C and O atoms were weighted 10% less the structure did not refine; the thermal parameters of the C atom became nonpositive definite. This result precludes the existence of $Ir(CO)_2Cl_2$

molecules within the material and agrees with the previous Mössbauer and magnetic data.[5] The ligands around Ir(1) show no disorder. (4) The bond distances of the ligands bonded to Ir(1) and Ir(2) are shown in Figure 2. The Ir–CO distances give indications of multiple-bond character. The Ir(1)–CO bond which is trans to the Cl bond is 0.071 (8) Å shorter than the cis Ir–CO distance. This is consistent with a strong trans bond and a large backbonding $d\text{-}\pi_{\pi^*}$ contribution. (5) Unlike the Pt 1-D materials where water molecules and counterions fit into holes or channels in the lattice, $Ir(CO)_3Cl$ crystallizes in a close-packed lattice where all intermolecular contacts except for the Ir–Ir bond are at normal van der Waals distances. This leaves no room for interstitial Cl^- sites as can be verified by inspection of Figure 1. This is confirmed by the final difference Fourier map which showed no electron density above 0.6 $e^-/Å^3$ where 0.4 $e^-/Å^3$ was the noise level of the map.[13] A three-dimensional model based on van der Waals distances also shows no possible Cl^- sites; thus there are no holes or channels for disordered interstitial Cl^- ions within the lattice.

Therefore, based on the above structural and analytical evidence, we conclude that the earlier chemical analyses of Hieber[2] and later of Fischer[3] were correct and that $Ir(CO)_3Cl$ is stoichiometric. This finding is highly significant in view of the considerable evidence that this material has some of the properties of a metal or semimetal, e.g., its metallic luster, high conductivity, and linear metal chains with very short metal-metal bonds. However the physical measurements made on good samples of this material are rather meager as yet and proof of metallic character is lacking. If $Ir(CO)_3Cl$ is indeed a one-dimensional metal or semimetal, it would represent the first member of a new class of 1-D materials where the metallic state is stabilized by metal–metal and metal–ligand bonding without charge transfer to the lattice. Assuming that to be true an overlapping $5d_z2\text{-}6p_z$ band model offers a possible electronic description of the origin of the conduction band. Of course extensive calculations would be necessary to bear this out. Polarized reflectance measurements, x-ray diffuse scattering studies, and inelastic neutron scattering studies are being carried out to determine the metallic state of $Ir(CO)_3Cl$.

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(12) Because of the large correlations between the Cl(2) and C(4) atoms, the position and anisotropic thermal parameters of C(4) were fixed. The multipliers of Cl(2), C(4), and O(4) refined to 0.25(1), 0.25(2), and 0.25(1) respectively at an R_F 0.019.

(13) The calculated peak electron density for the 0.8 Cl atoms ($Z = 8$) disordered over 16-fold general positions is 0.85 $e^-/Å^3$. This value is obtained by direct scaling from the Cl(1) peak height on the final observed Fourier map.

(14) Participant in the Undergraduate Research Participation Program sponsored by the Argonne Center for Educational Affairs from Central Michigan University, Mt. Pleasant, Mich., 48859.

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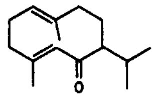
Received December 16, 1976

An Expeditious Route to the Germacranes. Total Synthesis of (±)-Acoragermacrone and (±)-Preisocalamendiol

Sir:

The germacranes are a class of commonly occurring medium-ring sesquiterpenes whose members include a variety of pheromones, antibiotics, cytotoxins, and antitumor agents.[1] These compounds are also known to be synthetic as well as biogenetic precursors of other important classes of sesquiterpenes.[2] Although a great deal of effort has been devoted to preparation of the requisite 1,5-cyclodecadiene ring,[3] only a few approaches have proven applicable to the synthesis of these chemically and thermally labile natural products.[4] Since existing syntheses either start from another relatively complex natural product (note exceptions[4d,e]) or suffer somewhat in terms of overall efficiency, we have conducted studies directed toward efficient new synthetic solutions to the germacranes. We wish to report (1) a concise and highly stereoselective approach to the 1,5-cyclodecadiene ring system from a simple monocyclic precursor; and (2) application of the sequence to total syntheses of (±)-acoragermacrone[5] (**1**) and (±)-preisocalamendiol[4c,6] (**2**).



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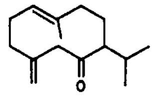

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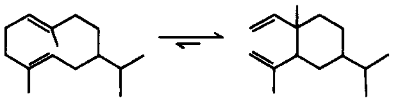
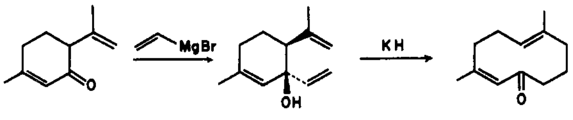
Our approach to 1,5-cyclodecadienes is based on the well-known tendency of the germacranes (i) to undergo an extemely facile Cope rearrangement to the isomeric elemane sesquiterpenes (ii).[7] Although the equilibrium usually lies toward ii, it is possible to upset the normal equilibrium and thus prepare 1,5-cyclodecadienes from appropriately substituted divinylcyclohexanes.



i **ii**

The starting point for our studies was the monoterpene isopiperitenone (**3**) which is itself readily prepared by oxidation of limonene.[8] Addition of vinylmagnesium bromide (THF, −20 °C) gave the *trans*-divinylcyclohexenol **4** (ir (neat) 3480 cm^{-1}), which was not purified but immediately subjected to the Evans modification[9] of the oxy-Cope rearrangement (KH, THF, 18-crown-6, 18 h, 25 °C).[10] Workup and short column chromatography gave a 75% overall yield of the (*Z*,*E*)-cyclodecadienone **5** (mp (pentane) 28.5–29 °C; IR (neat) 1685, 1635 cm^{-1}; NMR (δ^{CCl_4}) 5.93 (1 H, br s), 4.88 (1 H, br t, $J = 7$ Hz), 1.76 (3 H, d, $J = 1.2$ Hz), 1.43 (3 H, d, $J = 1.2$ Hz)). Spectral comparisons[3c] as well as NOE experiments confirmed the olefinic geometries shown. No trace of other isomers could be detected in the crude product.



3 **4** **5**

Although some germacranes incorporate the *Z*,*E* olefinic stereochemistry of **5**, most have the isomeric *E*,*E* geometry. It would therefore be desirable to have some method for isomerizing the more stable[5] *Z* enone **5** to the less stable *E* enone **6**. Although the usual procedures for olefin inversion via photoisomerization or intermediate epoxide opening proved ineffective, we felt that the conformational properties of the