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A Novel Tridentate Ligand Formed by the Condensation of Two Benzoyl Isothiocyanate Molecules in the Presence of $RhCl(PPh_3)_3$

Sir:

We wish to describe the preparation and characterization of a novel complex of Rh(III) in which a new tridentate ligand, formed by the condensation of two molecules of benzoyl isothiocyanate, is attached to the metal through S, C, and O linkages.

A mixture of $RhCl(PPh_3)_3$ (0.325 mmol) and excess benzoyl isothiocyanate (2.84 mmol) in a 1:1 benzene-hexane mixture (by volume) was kept at room temperature under nitrogen for 14 hr and then refluxed for 1 hr, giving a yellow-orange powder in 84% yield. Recrystallization of the crude product from mixed solvent (1:1 methylene chloride-diethyl ether) yielded a reddish orange microcrystalline solid, mp 174.5-175.5°, after 1 day. The analysis of these crystals is consistent with the formula, $RhCl(PPh_3)_2(C_6H_5CO\text{-}NCS)_2$: Anal. Calcd: C, 63.13; H, 4.08; N, 2.83. Found: C, 63.28; H, 4.18; N, 2.91. The NMR spectrum in $CDCl_3$ shows no sign of diethyl ether or methylene chloride. However, when the crude complex was recrystallized slowly, over a few days, from methylene chloride-diethyl ether, reddish orange prismatic crystals, mp 176-177°, were obtained which contained incorporated diethyl ether, as seen in the NMR spectrum (τ_{Me} 8.8). NMR and infrared studies of the product did not lead to a ready formulation of the nature of the complex. Accordingly an X-ray diffraction investigation was undertaken.

$RhCl(PPh_3)_2(PhCONCS)_2 \cdot Et_2O$ (Ph = C_6H_5, Et = C_2H_5) crystallizes in the space group C^5_{2h}-$P2_1/n$ with four formula units of the complex and four solvent molecules in a cell of dimensions a = 21.184 (3) Å, b = 19.963 (2) Å, c = 12.226 (2) Å, β = 100.03 (1)°, and V = 5091.56 Å^3. The experimental and calculated densities are 1.39 (1) and 1.387 g cm^{-3}, respectively.

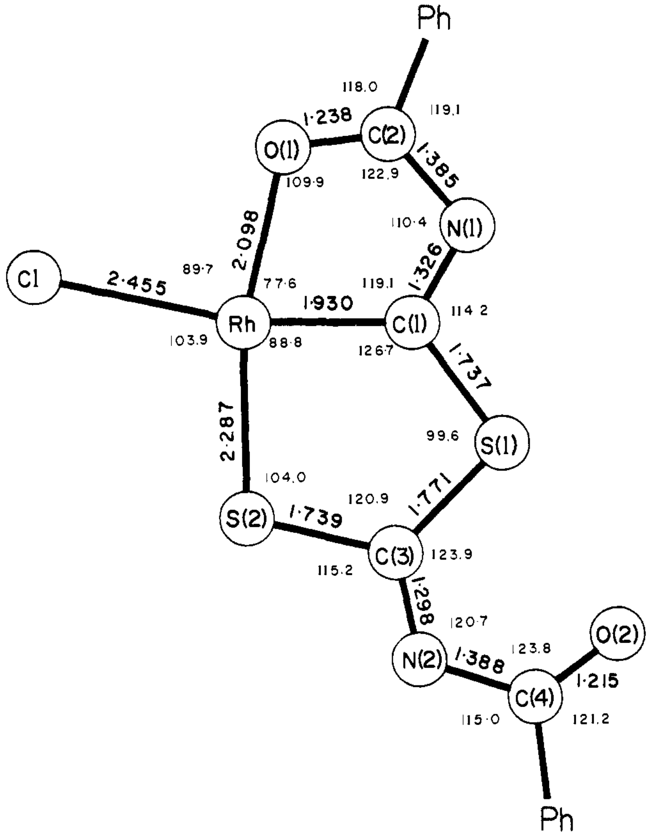

Figure 1. A drawing of $RhCl(PPh_3)_2(PhCONCS)_2$ viewed in the isothiocyanate ligand plane, showing important bond distances and angles. PPh_3 groups, approximately perpendicular to this plane, are omitted for clarity. Standard deviations in the bond lengths (in Å × 10^3) are: Rh-Cl, 2; Rh-O, 2; Rh-C, 6; Rh-S, 2; C-O, 8; C-N, 8; S-C, 7.

Data were collected on a Picker X-ray diffractometer, using nickel-filtered Cu Kα radiation. Of the 8248 unique reflections measured, 6266 were significantly above background ($F_o^2 > 3\sigma(F_o^2)$). The absorption-corrected data have been refined by full-matrix least-squares methods to an R of 0.061 and R_w of 0.079. The diethyl ether molecule was found to be severely disordered.

Fractional coordinates for the individual atoms and positional parameters for the rigid groups appear in Tables I and II in the microfilm edition.[1]

The Rh atom has a slightly distorted octahedral coordination with trans PPh_3 groups in the axial positions. The four equatorial sites are occupied by a chloro ligand and the tridentate ligand $(PhCONCS)_2$. Figure 1 shows the molecule viewed in the isothiocyanate ligand plane, with relevant bond lengths and angles shown. The PPh_3 groups, approximately perpendicular to this plane, are omitted for the sake of clarity.

This tridentate ligand is an interesting and unexpected consequence of the aforementioned reaction. Although the five-membered ring formed by Rh, O(1), C(2), N(1), and C(1) is not surprising, on the basis of the previous work on benzoyl and thiobenzoyl isocyanates,[2] the condensation of the two ligands at C(3)-S(1) is without precedent. This sulfur-carbon bond joining the two ligands is a regular S-C single bond agreeing well with the distance of 1.77 Å based on the sums of the C and S covalent radii.[3,4]

The Rh-C(1) bond is believed to be the shortest Rh(III)-C(carbene) bond yet observed, being, for example, significantly shorter than the distances of 1.968 and 1.961 Å observed in RhI$_3$(CO)CPhNMeCPhNMe,[5] and RhCl$_3$(CHNMe$_2$)(PEt$_3$)$_2$,[6] respectively. It is also significantly shorter than other Rh(III)-C(alkyl) single bond distances (2.05-2.08 Å)[7-10] even allowing for the change in covalent radius from C(sp^2) to C(sp^3). The shortness of the Rh-C bond may result from increased back-donation from metal d to the p$_z$ orbital on the trigonal carbon atom. It may also result from ligand constraints. Although short, this Rh-C distance is still longer than the Rh(III)-C(carbonyl) distance (1.89 Å) observed in the rhodium carbonyl complex mentioned above.[5]

The carbene carbon atom has the expected high trans influence, resulting in a Rh-Cl bond which is longer than those observed when chlorine is trans to another chlorine ligand[11] (2.34 Å) or to pyridine[7] (2.339 Å). However, it is shorter than the Rh-Cl distance of 2.531 Å observed when a benzyl carbon atom is the trans ligand.[7]

Within the metallocyclic rings there is some delocalization evident as witnessed by the C(2)-O(1) and C(1)-N(1) bonds being longer than the double bond values (compare C(4)-O(2) and C(3)-N(2)). Similarly N(1)-C(2) is shorter than a C-N single bond (1.43 Å). In the ring involving Rh, C(1), S(1), C(3), and S(2) the C(1)-S(1) and C(3)-S(2) bonds are both intermediate between single and double bonds so here again the possibility of delocalization exists.

The ring involving Rh, C(1), N(1), C(2), and O(1) is essentially planar with only C(2) being displaced by 0.015 Å from the mean plane. The Rh-S(2)-C(3)-S(1)-C(1) ring is slightly puckered with C(3) and C(1) deviating from the mean plane by 0.032 and −0.039 Å, respectively. The stability of this complex may arise in part from resonance stabilization resulting from the extended π system on the ligand and on the nearly coplanar phenyl groups.

Analogous reactions involving benzoyl isocyanate in place of benzoyl isothiocyanate yield five-membered metallocyclic structures, as determined in a routine matter spectroscopically. The present results illustrate the striking differences that may be expected between reactions of isocyanates and isothiocyanates with low-valent transition metal systems.

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Supplementary Material Available. Tables I and II will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number JACS-75-4748.

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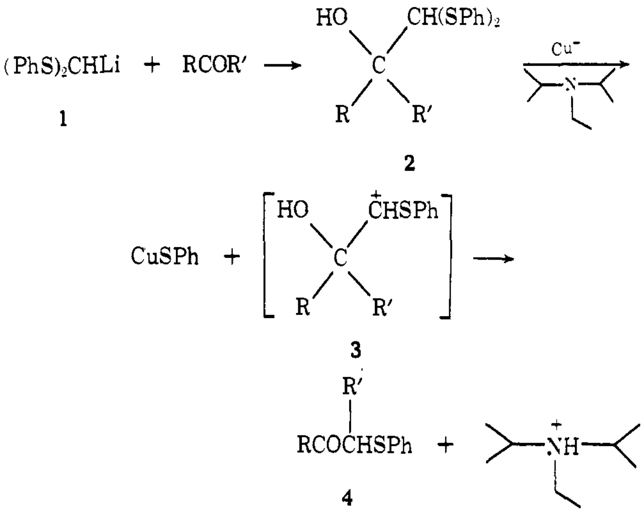
Application of Copper(I)-Induced Thiophenoxide Removal to Ring Expansions or Chain Extensions of Aldehydes and Ketones. Detection, Isolation, and Independent Preparation of the α-Epoxy Thioether Intermediate

Sir:

Recent work from this laboratory[1] has demonstrated that sulfur-stabilized carbonium ions can be readily generated in organic solvents under mild conditions by removal of a thiophenoxide ion from a thioacetal or thioketal using soluble cuprous trifluoromethanesulfonate (triflate).[2] The procedure was applied to the syntheses of a variety of vinyl sulfides and of a furan. We now report applications which result in new synthetic procedures and which illustrate the high selectivity of the process.

The α-hydroxydiphenylthioacetals (**2**, 3 mmol in a typical run), readily obtained by the addition of the lithio derivative (**1**) of dithiophenoxymethane to aldehydes and ketones,[3] react with cuprous triflate (6 mequiv) in benzene (15 ml) containing diisopropylethylamine (4 mmol) to give, in most cases, good yields of rearrangement products, **4**, presumably via the intermediate cation **3**.[4]



The procedure provides a method for producing the homologous α-thiophenoxy ketones and it results in ring expansion in the case of cyclic ketones (Table I). The ketonic products thus functionalized are exceedingly useful synthetic intermediates[5] and some would be difficult to prepare by available procedures. This overall insertion process should thus find use in synthesis. Although a number of ring-expansion procedures for ketones are available, none of them lead directly to 2-sulfenylated ketones and most suffer by comparison with the present method with regard to ease of operation and yield.[6,7]