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# A Tridentate Ligand Formed by the Condensation of Two Benzoyl Isothiocyanate Molecules in the Presence of $RhCl(P(C_6H_5)_3)_3$. Structure of $RhCl((C_6H_5)CONCS)_2(P(C_6H_5)_3)_2{\cdot}(C_2H_5)_2O$

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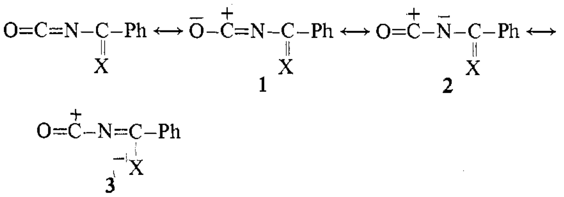
The structure of $RhCl((C_6H_5)CONCS)_2(P(C_6H_5)_3)_2{\cdot}(C_2H_5)_2O$ has been determined crystallographically. The rhodium atom in the complex possesses pseudooctahedral geometry with trans phosphine ligands in the axial positions and the four equatorial positions being occupied by a chloro and a tridentate ligand, $((C_6H_5)CONCS)_2$. This novel ligand is formed by the condensation of two benzoyl isothiocyanate molecules joined together at the sulfur atom of one ligand and the isothiocyanate carbon atom of the second. The resulting ligand is bonded to the rhodium atom via a sulfur atom, a carbon atom, and an oxygen atom forming two fused five-membered metallocycles sharing the rhodium atom and the carbene carbon atom along a common edge. Bond lengths within the resulting chelate rings are intermediate between single- and double-bonded values and therefore suggest delocalization over the ligand framework. In addition the entire ligand is essentially planar thus facilitating any delocalized bonding. The Rh–C(carbene) bond (1.930 (6) Å) is the shortest rhodium–carbene distance yet observed and this carbene shows a strong trans influence resulting in a long Rh–Cl bond length of 2.455 (2) Å. The diethyl ether molecules, which are located in the cavities between the triphenylphosphine and $((C_6H_5)CONCS)_2$ ligands, are severely disordered and thus no satisfactory description of these molecules is possible. The complex crystallizes from methylene chloride–diethyl ether as bright orange prisms containing solvated diethyl ether. The space group is $C_{2h}^5$-$P2_1/n$ with $a$ = 21.184 (3) Å, $b$ = 19.963 (2) Å, $c$ = 12.226 (2) Å, $\beta$ = 100.03 (1) °, $V$ = 5092 Å$^3$, and $Z$ = 4. Based on 6266 unique reflections with $F_o^2 \geq 3\sigma(F_o^2)$ the structure was refined by full-matrix, least-squares techniques to give $R$ = 0.061 and $R_w$ = 0.079. The Rh–S and Rh–O distances are 2.287 (2) and 2.098 (4) Å, respectively.

## Introduction

Recently the reactions of low-valent transition metal complexes, notably of Rh(I) and Pd(0), with benzoyl isocyanates and thiobenzoyl isocyanates have been reported.[1] The resulting products form an interesting series of compounds in which the isocyanate ligands can coordinate to the metal in a variety of ways. The possible coordination sites of the ligand can be seen in the canonical structures (X = O or S; Ph = $C_6H_5$)



$$\mathrm{O{=}C{=}N{-}\underset{\underset{X}{\|}}{C}{-}Ph \longleftrightarrow \overset{-}{O}{-}\overset{+}{C}{=}N{-}\underset{\underset{X}{\|}}{C}{-}Ph \longleftrightarrow O{=}\overset{+}{C}{-}\overset{-}{N}{-}\underset{\underset{X}{\|}}{C}{-}Ph \longleftrightarrow}$$

1 2

$$\mathrm{O{=}\overset{+}{C}{-}N{=}\underset{\underset{{}^{-}X}{|}}{C}{-}Ph}$$

3

Coordination via mode **1** would result in a three-membered $\overline{\mathrm{M{-}C{-}O}}$ ring in which the metal bridges the C–O bond. A similar coordination has been observed or postulated in several $CS_2$ complexes,[2-4] where the metal instead bridges a C–S bond. Also in $RhCl(SCNPh)_2(PPh_3)_2$ one isothiocyanate ligand was postulated as being bidentate, forming a $\overline{\mathrm{Rh{-}C{-}S}}$ ring analogous to mode **1**, whereas the second isothiocyanate ligand was believed to be bonded end-on through the sulfur atom.[4] Coordination by mode **2** results in a $\overline{\mathrm{M{-}C{-}N}}$ ring with the metal bridging the C–N bond. Collman et al. have postulated[5] a structure of this type in $IrCl(PhCONCO)(PPh_3)_2$. The third possibility, shown by mode **3**, yields a five-membered ring with either a $\overline{\mathrm{M{-}C{-}N{-}C{-}O}}$ or a $\overline{\mathrm{M{-}C{-}N{-}C{-}S}}$ skeleton, resulting from 1,4 addition of the ligand. There is much current interest in five-membered metallocyclic complexes which contain heteroatoms (usually O and N), and compounds of this type have been prepared, for example, with azobenzene,[6] *N*-benzoylhydrazine,[7] dibenzoylhydrazine,[8] and imidoyl chloride,[9] resulting in either $\overline{\mathrm{M{-}N{-}N{-}C{-}C}}$, $\overline{\mathrm{M{-}N{-}N{-}C{-}O}}$, or $\overline{\mathrm{M{-}N{-}C{-}N{-}C}}$ skeletons. However until recently no complexes had been prepared which contain a skeleton of the type formed by coordination mode **3**.

A natural extension of this work, the investigation of benzoyl isothiocyanate as a ligand, might be expected to yield a range of complexes with coordinations similar to those of the corresponding (thio)benzoyl isocyanates, as is shown in schemes **1**–**3**. However, based on an ir investigation,[10] the coordination of PhCONCS in $RhCl(PhCONCS)_2(PPh_3)_2$ could not be simply correlated with the analogous isocyanates. The x-ray structural determination of $RhCl(PhCONCS)_2(PPh_3)_2$ was therefore undertaken as part of a study of the coordination of isocyanate and isothiocyanate ligands and was used to ascertain which, if any, of the above coordination modes is present in this complex. A preliminary communication of this work has appeared.[11] Here we extend that report and discuss the structure in more detail.

## Experimental Section

Clear orange crystals of $RhCl(PhCONCS)_2(PPh_3)_2$, which were kindly supplied by Professor Y. Ishii, crystallize from 1:1 methylene chloride–diethyl ether with four molecules of complex and four molecules of diethyl ether in the lattice. Preliminary photography (oscillation and Weissenberg) showed Laue symmetry $2/m$. Systematic absences, as determined from $hk0$ and $hk1$ Weissenberg and $h0l$ and $h1l$ precession photographs, all using Ni-filtered Cu K$\alpha$ radiation, are $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with the monoclinic space group $C_{2h}^5$-$P2_1/n$. Precise lattice parameters at 22 °C were obtained by a least-squares refinement of the setting angles of 14 reflections ($50.6° \leq 2\theta \leq 56.4°$) which had been centered on the Cu K$\alpha_1$ peak (1.54056 Å) using a narrow source. These are $a$ = 21.184 (3) Å, $b$ = 19.963 (2) Å, $c$ = 12.226 (2) Å, $\beta$ = 100.03 (1)°, $V$ = 5092 Å$^3$. The experimental density (1.39 (1) g cm$^{-3}$), measured in aqueous KI, agrees well with the value of 1.387 g cm$^{-3}$ calculated for four formula units in the cell. The presence of ether of crystallization was verified by NMR measurements on a $CDCl_3$ solution of the sample, performed on a Perkin-Elmer R20B spectrometer. The expected methyl triplet and methylene quartet were observed at $\tau$ 8.89 and 6.58, respectively, with respect to TMS.

Data were collected on a Picker FACS-I computer-controlled x-ray diffractometer, equipped with a scintillation counter and pulse height analyzer, which was set to accept 90% of the Cu K$\alpha$ peak. The mosaicity of the crystal was judged acceptable using an $\omega$ scan with a narrow source and open counter. A $\theta$–$2\theta$ scan technique using Ni-filtered Cu radiation and a takeoff angle of 3.8° was employed

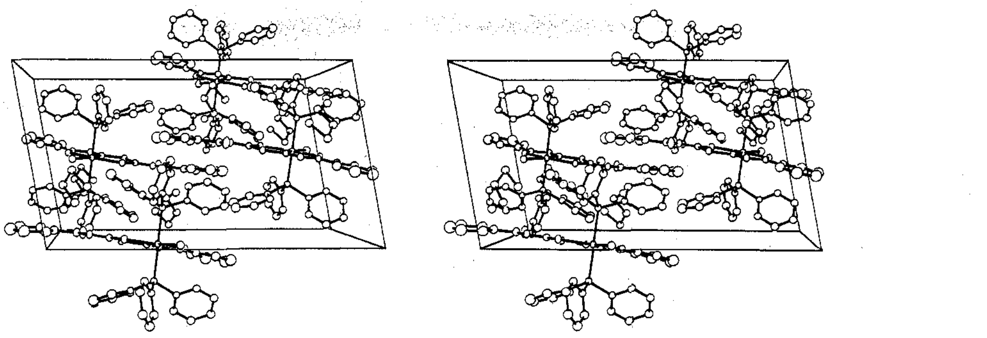


**Figure 1.** Stereodrawing of a unit cell of $RhCl(PhCONCS)_2(PPh_3)_2{\cdot}Et_2O$. The *x* axis is horizontal to the right; the *y* axis is perpendicular to the paper going away from the reader, and the *z* axis is almost vertical. Vibrational ellipsoids are drawn at the 20% level except for atoms in the ethyl ether molecule which are drawn arbitrarily small for clarity.

to collect all unique reflections with $2\theta$ less than 123°. The counter was positioned 30 cm from the crystal with the counter aperture 3.5 mm wide and 3.8 mm high. Copper foil attenuators were automatically inserted if the diffracted beam exceeded about 7000 Hz. Reflections were scanned at 2° $min^{-1}$ from 0.9° below the $K\alpha_1$ to 0.9° above the $K\alpha_2$ peak. Background counts were measured for 10 s at the limits of the scan. Seven standard reflections were measured every 100 reflections to assess decomposition or crystal movement. No significant variation in the standards was observed. The 8248 independent reflections measured were reduced to 6266 which were significantly above background ($F_o^2 \geq 3\sigma(F_o^2)$). Standard deviations in the observed intensities were calculated as described previously[12] using a value of 0.03 for *p*.

The crystal faces were found to be of the forms {110}, {011}, {100}, and {010} with dimensions along the direct crystal axes of 0.17 × 0.19 × 0.63 mm.

## Solution and Refinement of Structure

The structure was refined using full-matrix, least-squares techniques,[13] minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weight, *w*, is $4F_o^2/\sigma^2(F_o^2)$. The agreement indices *R* and $R_w$ are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2)^{1/2}$. The atomic scattering factors used for Rh, Cl, S, P, O, N, and C were those of Cromer and Waber,[14] whereas the values used for hydrogen were by Stewart et al.[15] Anomalous dispersion terms of Cromer and Liberman[16] for Rh, Cl, S, and P were applied to the calculated structure factors.

From a sharpened, origin-removed Patterson synthesis it was possible to locate the Rh atom plus five additional positions corresponding to the Cl, P, and S atoms. These five lighter atoms could not be distinguished at this stage so they were included as five sulfur atoms with the Rh atom in a least-squares cycle of refinement. The resulting agreement indices were $R = 0.39$ and $R_w = 0.48$. An ensuing electron density difference map led to positions for all other nonhydrogen atoms of the complex, and the differentiation among the Cl, S, and P atoms was then readily made. One cycle of refinement with the carbon atoms of the phenyl groups constrained to their well-known geometry and refined as rigid bodies with a C–C distance of 1.392 Å and with all other atoms refined isotropically yielded values of $R = 0.111$ and $R_w = 0.150$.

An absorption correction was applied to the data using a linear absorption coefficient of 49.8 $cm^{-1}$. The resulting transmission factors ranged from 0.361 to 0.574. The next cycle of refinement, in which all nongroup atoms were allowed to vibrate anisotropically, led to values of $R = 0.074$ and $R_w = 0.103$. Next an electron density difference map showed a large region of density having the approximate external dimensions of a diethyl ether molecule with no clearly defined maxima. Presumably the ether molecule is disordered. Nevertheless positions of the carbon and oxygen atoms were estimated and these positions, along with isotropic thermal parameters, were included among the variables refined in ensuing cycles. The hydrogen atom positions of the phenyl groups were calculated from the rigid-body parameters using a C–H distance of 0.98 Å. Each hydrogen atom was given a thermal parameter 1 $Å^2$ greater than that of its attached carbon atom. Two final cycles of refinement with the hydrogen atoms of the phenyl groups added as a fixed contribution to the structure factor calculations led to the agreement indices $R = 0.061$ and $R_w = 0.079$. In the final least-squares refinement, 243 parameters were varied and the error in an observation of unit weight was 3.03 electrons, based on 6266 observations. Refinement was concluded at this time because all major shifts were associated with the ether molecule with no significant shifts in the rest of the structure.

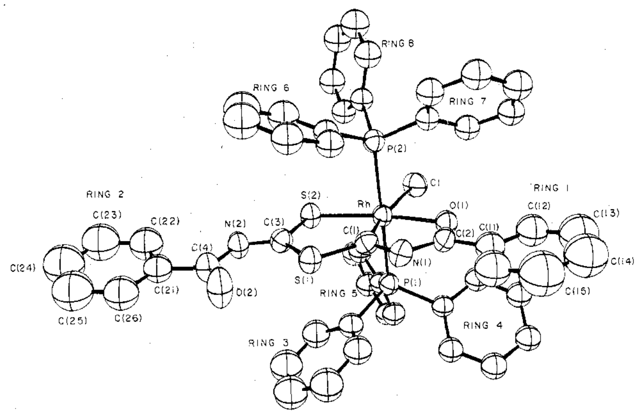


**Figure 2.** Molecule of $RhCl(PhCONCS)_2(PPh_3)_2$ showing the numbering scheme used. Hydrogen atoms are omitted for clarity of the drawing. Vibrational ellipsoids are drawn at the 50% level.

Analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of setting angles, $|F_o|$, and Miller indices showed no unexpected trends. However, the analysis as a function of $\theta$ revealed poor agreement at low angles owing to an inadequate description of the diethyl ether molecule. Yet, the final analysis was significantly improved over an analysis performed before inclusion of the solvent molecule. In the final difference Fourier map the largest peaks were associated with the phenyl rings (1.0–0.7 e $Å^{-3}$) and with the ether (0.7 e $Å^{-3}$). A typical phenyl carbon atom had a height of 4.4 e $Å^{-3}$. Of the 1982 unobserved reflections, 27 have $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$ and 15 have $|F_o^2 - F_c^2| > 5\sigma(F_o^2)$.

The final atomic positional and thermal parameters along with their standard deviations, as estimated from the inverse matrix, are given in Table I. Table II lists the positional parameters of the eight phenyl groups and the carbon atom positions derived from these rigid-body parameters, together with the isotropic thermal parameters of these carbon atoms. The idealized hydrogen atom positions for the phenyl rings are shown in Table III.[17] The final values of $10|F_o|$ and $10|F_c|$ in electrons are given in Table IV,[17] and the root-mean-square amplitudes of vibration are listed in Table V.[17]

## Description of Structure and Discussion

The unit cell consists of four monomeric molecular units with four disordered diethyl ether groups fitting into cavities created by the $PPh_3$ groups and the isothiocyanate ligands. This is shown in the stereoscopic view of the molecular packing in Figure 1. All intermolecular contacts are normal, being approximately equal to the van der Waals contacts. The numbering scheme is shown on the three-dimensional view of the molecule in Figure 2. Figure 3 represents the molecule viewed in the isothiocyanate ligand plane, showing the important bond distances and angles.

The Rh atom has a slightly distorted octahedral coordination with trans $PPh_3$ groups being in the axial positions and the

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $RhCl(PPh_3)_2(PhCONCS)_2 \cdot Et_2O$

| ATOM | X[A] | Y | Z | B11[B] OR B,A$^2$ | B22 | B33 | B12 | B13 | B23 |
|---|---|---|---|---|---|---|---|---|---|
| RH | 0.329733(21) | 0.070150(24) | 0.01792(4) | 16.62(12) | 23.61(14) | 62.6(4) | 1.38(10) | 5.05(15) | 0.43(19) |
| S(2) | 0.23181(8) | 0.03435(8) | 0.04874(15) | 19.0(4) | 25.5(5) | 89.1(16) | 1.3(3) | 9.4(6) | 2.3(7) |
| P(1) | 0.36270(8) | 0.08106(8) | 0.21301(14) | 18.9(4) | 26.5(5) | 63.8(13) | 2.0(4) | 4.9(6) | 0.5(6) |
| CL | 0.39325(8) | -0.03312(9) | 0.02465(15) | 26.6(5) | 30.7(5) | 86.7(15) | 7.6(4) | 5.6(7) | 0.2(7) |
| S(1) | 0.22078(8) | 0.18620(8) | 0.02261(15) | 20.1(4) | 25.2(5) | 86.3(15) | 1.3(3) | 7.7(6) | 2.4(7) |
| P(2) | 0.29627(8) | 0.05269(8) | -0.17614(14) | 18.9(4) | 23.7(5) | 66.4(14) | 1.0(3) | 5.3(6) | -0.8(6) |
| O(1) | 0.40934(20) | 0.12543(23) | -0.0115(4) | 19.3(11) | 30.0(15) | 68.(4) | 0.7(10) | 6.4(16) | 0.6(19) |
| N(1) | 0.33496(25) | 0.20995(28) | -0.0143(5) | 21.5(15) | 26.7(17) | 83.(5) | -2.3(13) | 5.8(22) | 1.0(23) |
| C(2) | 0.3950(3) | 0.1854(4) | -0.0236(6) | 18.4(17) | 35.7(25) | 63.(5) | -4.0(16) | 3.3(23) | -2.(3) |
| C(1) | 0.2967(3) | 0.1605(3) | 0.0053(5) | 21.5(17) | 24.5(19) | 63.(5) | 0.8(15) | 1.7(24) | 1.0(25) |
| C(3) | 0.1875(3) | 0.1077(3) | 0.0487(6) | 20.8(18) | 24.2(19) | 71.(6) | 1.5(14) | 3.7(25) | 2.0(26) |
| N(2) | 0.12946(25) | 0.09985(28) | 0.0674(5) | 18.4(14) | 27.9(17) | 96.(6) | 2.0(13) | 10.6(22) | 0.0(25) |
| O(2) | 0.10697(25) | 0.21245(28) | 0.0662(6) | 25.8(15) | 29.8(18) | 214.(8) | 1.7(13) | 24.1(28) | 9.(3) |
| C(4) | 0.0898(3) | 0.1547(4) | 0.0724(7) | 22.8(19) | 31.0(24) | 102.(7) | 1.9(17) | 11.(3) | 5.(3) |
| C(5) | 0.4231(14) | 0.3772(14) | 0.2804(24) | 23.7(10) | | | | | |
| C(6) | 0.3887(15) | 0.3863(15) | 0.2470(27) | 33.8(11) | | | | | |
| O(3) | 0.4166(10) | 0.4536(10) | 0.1580(16) | 34.7(6) | | | | | |
| C(7) | 0.3470(12) | 0.4426(12) | 0.1672(20) | 30.0(8) | | | | | |
| C(8) | 0.3850(9) | 0.4996(10) | 0.0826(15) | 18.2(5) | | | | | |

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X $10^4$.

Table II. Derived Parameters for the Rigid-Group Atoms of $RhCl(PPh_3)_2(PhCONCS)_2 \cdot Et_2O$

| ATOM | X | Y | Z | B,A$^2$ | ATOM | X | Y | Z | B,A$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| C11 | 0.44374(25) | 0.2318(3) | -0.0497(5) | 5.50(17) | C51 | 0.36846(22) | 0.00349(19) | 0.2940(3) | 3.90(13) |
| C12 | 0.5025(3) | 0.20610(25) | -0.0658(5) | 6.63(20) | C52 | 0.33726(22) | -0.05501(24) | 0.2530(3) | 4.95(15) |
| C13 | 0.54855(24) | 0.2485(4) | -0.0965(6) | 9.7(3) | C53 | 0.34135(25) | -0.11209(19) | 0.3193(4) | 6.09(18) |
| C14 | 0.5358(3) | 0.3166(4) | -0.1111(7) | 10.5(3) | C54 | 0.37663(26) | -0.11067(20) | 0.4265(4) | 6.03(19) |
| C15 | 0.4771(4) | 0.34232(24) | -0.0950(6) | 11.3(4) | C55 | 0.40782(23) | -0.05216(25) | 0.4674(3) | 5.28(16) |
| C16 | 0.43104(27) | 0.2999(3) | -0.0643(6) | 7.54(23) | C56 | 0.40374(22) | 0.00492(19) | 0.4012(4) | 4.90(15) |
| C21 | 0.02391(24) | 0.1383(3) | 0.0865(5) | 5.51(17) | C61 | 0.22050(20) | 0.09421(22) | -0.2333(4) | 4.06(13) |
| C22 | 0.0029(3) | 0.07220(27) | 0.0835(6) | 7.83(24) | C62 | 0.21852(20) | 0.16233(22) | -0.2578(4) | 4.75(15) |
| C23 | -0.0607(4) | 0.0580(3) | 0.0901(7) | 10.1(3) | C63 | 0.16004(26) | 0.19347(19) | -0.2959(5) | 5.82(18) |
| C24 | -0.10321(26) | 0.1099(4) | 0.0996(7) | 11.2(4) | C64 | 0.10353(20) | 0.1565(3) | -0.3096(5) | 7.77(24) |
| C25 | -0.0822(3) | 0.1760(4) | 0.1026(6) | 10.3(3) | C65 | 0.10551(21) | 0.0884(3) | -0.2851(5) | 8.67(27) |
| C26 | -0.0186(4) | 0.19024(24) | 0.0960(6) | 7.55(23) | C66 | 0.16399(27) | 0.05723(19) | -0.2470(5) | 6.69(20) |
| C31 | 0.31010(23) | 0.13377(25) | 0.2800(4) | 4.72(15) | C71 | 0.35574(18) | 0.08225(22) | -0.2572(4) | 3.79(12) |
| C32 | 0.31256(25) | 0.20318(26) | 0.2711(4) | 5.86(18) | C72 | 0.41918(20) | 0.06411(22) | -0.2191(3) | 4.47(14) |
| C33 | 0.2725(3) | 0.24304(20) | 0.3227(5) | 7.76(24) | C73 | 0.46711(15) | 0.08516(24) | -0.2759(4) | 4.95(15) |
| C34 | 0.22995(28) | 0.2135(3) | 0.3831(5) | 8.14(25) | C74 | 0.45161(20) | 0.12435(25) | -0.3709(4) | 5.50(17) |
| C35 | 0.22749(26) | 0.1441(3) | 0.3919(5) | 8.17(25) | C75 | 0.38817(23) | 0.14250(24) | -0.4091(3) | 5.52(17) |
| C36 | 0.26757(27) | 0.10422(21) | 0.3403(5) | 6.17(19) | C76 | 0.34023(17) | 0.12145(23) | -0.3522(4) | 4.87(15) |
| C41 | 0.44281(16) | 0.11822(21) | 0.2478(4) | 3.73(12) | C81 | 0.28144(22) | -0.03320(18) | -0.2250(4) | 3.98(13) |
| C42 | 0.45752(19) | 0.16974(22) | 0.3247(4) | 4.70(15) | C82 | 0.27760(25) | -0.04557(23) | -0.3380(4) | 5.51(16) |
| C43 | 0.51959(22) | 0.19519(21) | 0.3480(4) | 5.31(16) | C83 | 0.25970(27) | -0.10868(27) | -0.3809(3) | 6.50(19) |
| C44 | 0.56695(16) | 0.16913(23) | 0.2944(4) | 5.08(16) | C84 | 0.24566(27) | -0.15942(20) | -0.3109(4) | 6.25(19) |
| C45 | 0.55224(18) | 0.11762(23) | 0.2175(4) | 5.04(15) | C85 | 0.24950(26) | -0.14705(20) | -0.1979(4) | 5.65(17) |
| C46 | 0.49018(21) | 0.09217(20) | 0.1942(3) | 4.59(14) | C86 | 0.26740(24) | -0.08394(24) | -0.15495(29) | 4.74(15) |

RIGID GROUP PARAMETERS

| GROUP | $X_C$[A] | $Y_C$ | $Z_C$ | DELTA[B] | EPSILON | ETA |
|---|---|---|---|---|---|---|
| RING1 | 0.48979(22) | 0.27421(24) | -0.0804(3) | 0.672(4) | -3.024(4) | -0.405(4) |
| RING2 | -0.03965(24) | 0.12412(25) | 0.0931(4) | 0.188(4) | -3.045(4) | 2.912(4) |
| RING3 | 0.27003(17) | 0.17363(21) | 0.3315(3) | 2.698(4) | -2.708(4) | 0.664(4) |
| RING4 | 0.50488(15) | 0.14368(15) | 0.27111(25) | -2.727(3) | 2.349(3) | 3.085(4) |
| RING5 | 0.37254(15) | -0.05359(16) | 0.36022(27) | -0.859(4) | -2.4340(28) | 0.850(4) |
| RING6 | 0.16201(17) | 0.12535(19) | -0.27144(29) | 2.645(3) | -3.003(3) | -0.182(3) |
| RING7 | 0.40367(15) | 0.10330(15) | -0.31406(26) | 0.963(3) | 2.5538(28) | -0.853(4) |
| RING8 | 0.26355(15) | -0.09631(17) | -0.26793(29) | 2.871(10) | -1.9070(27) | -1.555(10) |

[A] $X_C$, $Y_C$, AND $Z_C$ ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

four equatorial sites being occupied by the chloro ligand and the tridentate $(PhCONCS)_2$ ligand. This ligand is the surprising feature of the structure, having been formed by the condensation of two benzoyl isothiocyanate molecules at S(1)–C(3). The resulting ligand is unique in that it contains three heteroatoms (N, O, and S) and is bonded to the rhodium atom via a sulfur atom, a carbon atom, and an oxygen atom. The resulting two fused five-membered metallocycles share Rh and C(1) along a common edge.

The reaction producing this type of complex has been

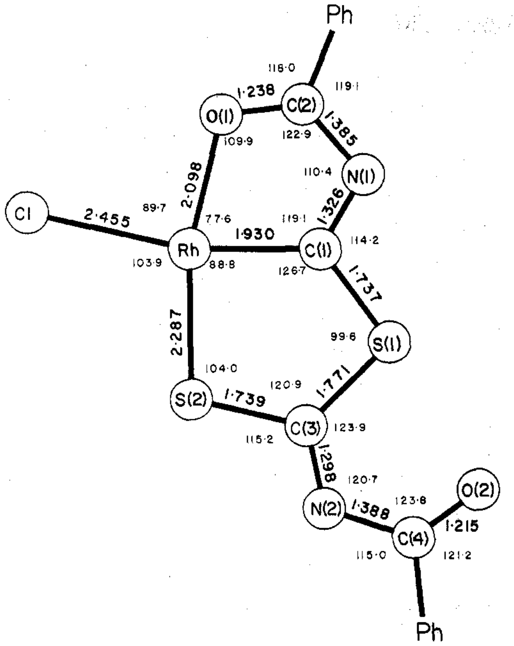


**Figure 3.** Representation of the molecule viewed perpendicular to the isothiocyanate ligand plane, showing important bond lengths and angles. $PPh_3$ groups, approximately perpendicular to this plane, are omitted for clarity.

**Table VI.** Selected Distances (Å) in $RhCl(PhCONCS)_2(PPh_3)_2{\cdot}Et_2O$

Bond Distances

| | | | | |
|---|---|---|---|---|
| Rh–Cl | 2.455 (2) | N(2)–C(4) | 1.388 (9) | |
| Rh–P(1) | 2.376 (2) | C(4)–O(2) | 1.215 (8) | |
| Rh–P(2) | 2.381 (2) | C(4)–C(21) | 1.473 (9) | |
| Rh–S(2) | 2.287 (2) | P(1)–C(31) | 1.827 (6) | 1.830 (6) |
| Rh–C(1) | 1.930 (6) | P(1)–C(41) | 1.830 (4) | |
| Rh–O(1) | 2.098 (4) | P(1)–C(51) | 1.833 (4) | |
| C(1)–N(1) | 1.326 (8) | P(2)–C(61) | 1.833 (4) | |
| C(1)–S(1) | 1.737 (7) | P(2)–C(71) | 1.831 (5) | |
| C(2)–N(1) | 1.385 (8) | P(2)–C(81) | 1.825 (4) | |
| C(2)–O(1) | 1.238 (8) | C(5)–C(6)[a] | 0.79 (4) | |
| C(2)–C(11) | 1.464 (9) | C(6)–O(3) | 1.89 (3) | |
| S(1)–C(3) | 1.771 (7) | O(3)–C(8) | 1.39 (2) | |
| S(2)–C(3) | 1.739 (7) | C(8)–C(7) | 1.82 (3) | |
| N(2)–C(3) | 1.298 (8) | | | |

Nonbonded Distances

| | | | |
|---|---|---|---|
| Rh–S(1) | 3.278 (2) | Cl–H(46) | 2.79 |
| S(2)–H(86) | 2.89 | O(1)–H(12) | 2.42 |
| S(2)–H(52) | 2.81 | O(1)–H(72) | 2.54 |
| Cl–H(86) | 2.82 | O(2)–H(26) | 2.52 |
| Cl–H(72) | 2.83 | N(1)–H(16) | 2.55 |
| Cl–H(52) | 2.79 | N(2)–H(22) | 2.45 |

[a] The diethyl ether molecule is numbered as C(5)–C(6)–O(3)–C(8)–C(7).

**Table VII.** Selected Angles (deg) in $RhCl(PhCONCS)_2(PPh_3)_2{\cdot}Et_2O$

| | | | |
|---|---|---|---|
| P(1)–Rh–P(2) | 176.82 (6) | C(3)–S(2)–Rh | 104.0 (2) |
| P(1)–Rh–Cl | 88.84 (6) | S(1)–C(3)–N(2) | 123.9 (5) |
| P(1)–Rh–O(1) | 91.1 (1) | S(2)–C(3)–N(2) | 115.2 (5) |
| P(1)–Rh–C(1) | 91.9 (2) | C(3)–N(2)–C(4) | 120.7 (6) |
| P(1)–Rh–S(2) | 88.84 (6) | N(2)–C(4)–O(2) | 123.8 (7) |
| P(2)–Rh–Cl | 88.67 (6) | N(2)–C(4)–C(21) | 115.0 (6) |
| P(2)–Rh–O(1) | 90.9 (1) | O(2)–C(4)–C(21) | 121.2 (7) |
| P(2)–Rh–C(1) | 90.9 (2) | C(4)–C(21)–C(22) | 120.9 (6) |
| P(2)–Rh–S(2) | 89.84 (6) | C(4)–C(21)–C(26) | 119.0 (6) |
| Cl–Rh–O(1) | 89.7 (1) | Rh–P(1)–C(31) | 114.0 (2) |
| Cl–Rh–S(2) | 103.86 (6) | Rh–P(1)–C(41) | 111.6 (2) |
| O(1)–Rh–C(1) | 77.6 (2) | Rh–P(1)–C(51) | 116.5 (1) |
| S(2)–Rh–C(1) | 88.8 (2) | Rh–P(2)–C(61) | 113.8 (2) |
| Rh–O(1)–C(2) | 109.9 (4) | Rh–P(2)–C(71) | 112.3 (1) |
| O(1)–C(2)–N(1) | 122.9 (6) | Rh–P(2)–C(81) | 117.9 (2) |
| C(2)–N(1)–C(1) | 110.4 (6) | C(31)–P(1)–C(41) | 106.0 (2) |
| Rh–C(1)–N(1) | 119.1 (5) | C(31)–P(1)–C(51) | 103.5 (2) |
| Rh–C(1)–S(1) | 126.7 (4) | C(41)–P(1)–C(51) | 104.2 (2) |
| N(1)–C(1)–S(1) | 114.2 (5) | C(61)–P(2)–C(71) | 106.7 (2) |
| O(1)–C(2)–C(11) | 118.0 (6) | C(61)–P(2)–C(81) | 102.2 (2) |
| N(1)–C(2)–C(11) | 119.1 (6) | C(71)–P(2)–C(81) | 102.8 (2) |
| C(2)–C(11)–C(12) | 118.7 (5) | C(7)–C(8)–O(3) | 54 (1) |
| C(2)–C(11)–C(16) | 121.2 (5) | C(8)–O(3)–C(6) | 134 (2) |
| C(1)–S(1)–C(3) | 99.6 (3) | O(3)–C(6)–C(5) | 96 (4) |
| S(1)–C(3)–S(2) | 120.9 (4) | | |

Torsion Angles

| | | | |
|---|---|---|---|
| Rh–P(1)–C(31)–C(36) | 103.7 (4) | Rh–P(2)–C(61)–C(66) | −97.4 (4) |
| Rh–P(1)–C(41)–C(42) | 133.6 (3) | Rh–P(2)–C(71)–C(76) | −133.0 (4) |
| Rh–P(1)–C(51)–C(56) | 162.6 (3) | Rh–P(2)–C(81)–C(82) | −164.3 (3) |
| C(31)–P(1)–P(2)–C(61) | −2.0 (3) | C(41)–P(1)–P(2)–C(71) | −0.8 (2) |
| C(51)–P(1)–P(2)–C(81) | −1.1 (3) | | |

termed[18-20] a "three-fragment oxidative addition" and is not without precedent.[9,18-21] For example, the coupling of two imidoyl ligands within the coordination sphere of a metal has been observed by Hitchcock, et al.,[9] in the reaction of an imidoyl chloride with $[RhCl(CO)_2]_2$ in the absence of HCl, affording a rhodium(III) carbene chelate $RhI_3(CO)CPhNMeCPhNMe$. As in the imidoyl chelate complex, we believe that, in the formation of $RhCl(PhCONCS)_2(PPh_3)_2$, first there is 1,4 addition of one isothiocyanate ligand to the metal followed by reaction of the resulting fragment with the second ligand to yield the present Rh(III)complex.

As in other carbene complexes,[22] the environment of the carbene carbon atom is clearly trigonal. Angles around this carbon atom are all close to the expected 120° (see Table VII). In addition C(1) is within 0.02 Å of the plane defined by Rh, S(1), and N(1). We believe that the Rh–C(1) bond, at 1.930 (6) Å, is the shortest $Rh^{III}$–C(carbene) bond yet observed. It may be compared with the distances 1.968 (13) and 1.961 (11) Å observed in the carbenes $RhI_3(CO)CPhNMeCPhNMe$[9] and $RhCl_3(CHNMe)(PEt_3)_2$.[23] In addition it is significantly shorter than the $Rh^{III}$–C distances (1.991 (9) and 1.984 (16) Å) observed in $Rh(O_2CMe)(N_2Ph_2)_2$[6] and $Rh(N_2Ph_2)_2Cl_2Ph(CO)_2$[24] and is also shorter than some $Rh^{III}$–C(alkyl) single-bond distances (2.05 (2)–2.08 (2) Å).[25-28] The shortness of this rhodium–carbene bond may be attributed to back-donation from filled metal d orbitals to the empty $p_z$ orbital on the trigonal carbon atom or perhaps to a steric effect of the ligand. In any event the Rh–C distance is longer than the $Rh^{III}$–C(carbonyl) distance of 1.892 (14) Å in the imidoyl complex.[9]

The carbene carbon atom shows the expected high trans influence, resulting in a Rh–Cl bond of 2.455 (2) Å, which is longer than those observed when the terminal chloro ligand is trans to another chloro ligand (2.29 (1)–2.364 (3) Å),[23,29-35] to a pyridine ligand (2.339 (4) Å),[25] or to a tertiary amine (2.33 (1) Å).[29] A compilation of several Rh–Cl distances is given in ref 24. The observed Rh–Cl distance in the isothiocyanate complex is very similar to that observed in $RhCl_3(CHNMe)(PEt_3)_2$ (2.445 (4) Å)[23] where the secondary carbene, –CHNMe, is in the trans position. Cetinkaya et al. have compared the trans influence of several ligands in octahedral Rh(III) systems, based on published $Rh^{III}$–Cl distances.[23] It is now possible to add a tertiary carbene to this series yielding the order $\sigma$-alkyl > $\sigma$-phenyl > *tert*-carbene > *sec*-carbene > *tert*-phosphine > *tert*-phosphite > *tert*-arsine ~ $\pi$-olefin > chlorine ~ amine ~ pyridine > ROH. The large trans influence displayed by the carbene in the present compound lends weight to the argument that the short Rh–C bond results from $d\pi$–$p\pi$ bonding rather than from a restricting effect of the chelate.

**Table VIII.** Deviations (Å $\times 10^3$) and Equations of Weighted Least-Squares Planes

Deviations

| Atom | Plane 1 | Plane 2 | Atom | Plane 1 | Plane 2 |
|---|---|---|---|---|---|
| Rh | −4 (3) | 19 (3) | C(1) | 1 (3) | −18 (3) |
| O(1) | 9 (3) | | S(1) | | 4 (3) |
| C(2) | −11 (3) | | S(2) | | −19 (3) |
| N(1) | 5 (3) | | C(3) | | 14 (3) |

Coefficients of the Plane Equation $AX + BY + CZ = D^a$

| Plane | $A$ | $B$ | $C$ | $D$ | |
|---|---|---|---|---|---|
| 1 | 2.617 | 2.634 | 11.158 | 1.259 | |
| 2 | 3.140 | 2.354 | 11.506 | 1.388 | |
| 3 | 4.471 | 3.218 | 11.157 | 2.175 | Phenyl 1 |
| 4 | 1.450 | −0.993 | 11.850 | 0.922 | Phenyl 2 |
| 5 | 2.313 | 0.589 | 11.729 | 1.149 | N(2), C(4), O(2) |

Dihedral Angles between Least-Squares Planes

| Plane A | Plane B | Angle, deg | Plane A | Plane B | Angle, deg |
|---|---|---|---|---|---|
| 1 | 3 | 5.40 | 2 | 5 | 5.58 |
| 1 | 2 | 1.63 | 4 | 5 | 5.11 |

[a] The plane is in crystal coordinates as defined by W. C. Hamilton, *Acta Crystallogr.*, 18, 502 (1965).

The Rh–S(2) bond, at 2.287 (2) Å, is short and indicative of some multiple-bond character. Thus in tris(dithioacetylacetonato)rhodium(III)[36] the average Rh–S distance is 2.321 (3) Å and in (*S*-methylethene-1,2-dithiolato)rhodium(III)[37] the Rh–S distances are 2.322 (3) and 2.369 (3) Å, all of which are significantly longer than found in the present determination. The Rh–O(1) bond (2.098 (4) Å) is not unusual, with Rh–O distances being reported[6,38–46] in the range 1.992 (3)–2.32 (2) Å. These limits obviously represent tightly and weakly bound ligands, respectively, and most determinations reported, involving acetato, oxalato, and aquo ligands, are intermediate between these extremes.

Both the Rh–C(1)–N(1)–C(2)–O(1) and the Rh–S(2)–C(3)–S(1)–C(1) rings are essentially coplanar (Table VIII). These planes are inclined to one another by only 1.63° so the inner coordination sphere of the chelate is nearly planar, leading to the possibility of delocalization over the ligand framework. Even the part of the ligand exo to the chelate is close to being coplanar with the rest of the ligand so any delocalization can extend to the phenyl rings. This can be seen in the bond lengths within the metallocycle rings. Both C(1)–N(1) and C(2)–O(1) (1.326 (8) and 1.238 (8) Å, respectively) are longer than the corresponding unchelated C(3)–N(2) and C(4)–O(2) distances (1.298 (8) and 1.215 (8) Å, respectively) whereas C(2)–N(1) at 1.385 (8) Å is shorter than the value of 1.43 Å expected for a C–N single bond. In the other ring the Rh–S(2) and Rh–C(1) distances (2.287 (2) and 1.930 (6) Å, respectively) are also indicative of some multiple bonding. The C(3)–S(2) and C(1)–S(1) bonds are also intermediate between C–S single bonds (1.77 Å) and C–S double bonds (1.61 Å) and are close to the formal double bonds in thiourea[47] (1.720 (9) Å) and its derivatives[48] (1.67 (2)–1.75 (1) Å).

Exo to the chelate ring the bond lengths are closer to those expected for a limiting valence-bond formulation, i.e., without significant contribution from delocalization. Thus the C(3)–N(2) bond at 1.298 (8) Å is very short and is similar to the C–N double bond in glyoxime (1.284 (4) Å).[49] In addition the C(4)–O(2) bond at 1.215 (8) Å is short and is similar to the formal C–O double bonds (1.19 (2) and 1.21 (2) Å) which are again exo to the chelate rings in $Mn(NH_2NHCO_2)\cdot 2H_2O$.[50] It is also shorter than the endocyclic C(1)-O(1) bond in the present compound (1.238 (8) Å).

The $PPh_3$ groups have their usual propeller configurations and are essentially eclipsed with torsion angles about the P–P axis which are close to 0° (see Table VII). In addition the pairs of phenyl groups which are eclipsed have similar torsion angles about the P–C bonds as is also shown in Table VII. Rings 3 and 6 have the largest such angles and are approximately parallel with the isothiocyanate ligand plane. The mutually trans Rh–P bond lengths agree well with the mutually trans Rh–P distances in other structures.[23,34,35] The P–C distances are all similar and have no unusual features. All thermal parameters in the phosphine phenyl rings are reasonable and show that these groups are well behaved.

As mentioned previously the diethyl ether molecules are disordered so the metric parameters shown in Tables VI and VII are unreliable.

In summary, although the benzoyl isothiocyanate molecule probably reacts via a 1,4 addition with $RhCl(PPh_3)_3$, as predicted by mode **3**, this product couples with an additional benzoyl isothiocyanate molecule to form a unique tridentate ligand. In this it differs from the reaction and bonding modes discussed above that have been postulated for the (thio)benzoyl isocyanate molecule.

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**Registry No.** $RhCl(PhCONCS)_2(PPh_3)_2\cdot Et_2O$, 57774-59-1.

**Supplementary Material Available:** Table III, the idealized positions of the hydrogen atoms, Table IV, observed and calculated structure amplitudes, and Table V, the root-mean-square amplitudes of vibration (45 pages). Ordering information is given on any current masthead page.

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# Structural and Dynamical Properties of Dicyclopentadienyltetracarbonyldiiron Derivatives with Linked Rings

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Previous studies of the fluxional processes (cis–trans isomerization and CO scrambling) in the cis and trans isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ (**1**, **2**) and various substitution products thereof, which lead to detailed mechanistic conclusions, have been extended to systems in which the $\eta^5\text{-}C_5H_5$ rings are linked. The systems now described are $(\eta^5\text{-}C_5H_4CMe_2CMe_2\text{-}\eta^5\text{-}C_5H_4)Fe_2(CO)_4$ (**6**), a derivative of **6** with $(PhO)_3P$ replacing a terminal CO (**7**), the azulenyl complex $(C_{10}H_8\text{–}C_{10}H_8)_2Fe_2(CO)_4$ (**8**), and a derivative of **8** with an $Fe(CO)_3$ group attached to the 1,3-butadiene portion of the seven-membered ring of each azulenyl group (**9**). The crystal structure of **8** has been determined. Bridge–terminal CO exchange occurs in **6** about as rapidly as in **1**, much more slowly in **8** and **9**, and not at all in **7**. These results are all in accord with the previously proposed mechanism which (1) requires bridged species to pass directly to staggered configurations of the nonbridged intermediates and (2) assumes the necessity of internal rotation in order for bridge–terminal exchange to be consummated. Crystallographic data for **8**: space group $C2/c$; $a = 8.971$ (2) Å, $b = 15.267$ (3) Å, $c = 14.316$ (2) Å, $\beta = 93.56$ (1)°, $Z = 4$. The structure was refined anisotropically to $R_1 = 0.029$ and $R_2 = 0.037$. The structure is derived from that of the cis isomer of **1** in an obvious way; it retains a $C_2$ symmetry axis and has Fe–Fe = 2.500 (2) Å. A comparison of the infrared spectrum of (**7**) with that of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_3P(OC_6H_5)_3$ indicated that the cis-bridged isomer of the latter compound is predominant in solutions in nonpolar solvents in contrast with $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ where the populations of cis- and trans-bridged isomers are almost equal at room temperature. A steric argument is proposed to account for this difference.

## Introduction

It has been known since 1970 that the cis and trans isomers of $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ (**1**, **2**) undergo rapid interconversion,[1] with an activation energy, as determined by proton NMR line shape analysis, of about 12 kcal $mol^{-1}$. The mechanism originally proposed involved passage through nonbridged intermediates (of which there are three, the enantiomorphous gauche rotamers, **3** and **4**, and the anti rotamer, **5**) and thus, as explicitly suggested,[1] the interchange of bridging and terminal carbonyl ligands should also occur rapidly. Within a very short time, Gansow, Burke, and Vernon[2] had confirmed this prediction by a $^{13}C$ NMR study of the same molecule. From the $^{13}C$ NMR data of Gansow et al., Adams and Cotton inferred a very detailed mechanistic hypothesis[3–6] to account for the relative rates of cis–trans interconversion, CO scrambling in the trans isomer, and CO scrambling in the cis isomer. A good deal of evidence has since been published to show that this mechanism, and no other, is correct.[4,7–9] More recently $^{13}C$ spectra of superior quality have been reported and used in a complete line shape analysis to evaluate the activation energy for bridge–terminal CO exchange, with the result $E_a = 11.7 \pm 1.0$ kcal/mol.[10]

In this paper we describe a number of additional confirmatory experiments, all centering around the concept of tying together the two $\eta^5\text{-}C_5H_5$ rings with two-carbon bridges so as to eliminate any trans-bridged isomer and to restrict the nonbridged isomers to only the gauche ones. The molecules dealt with are **6**–**9**. Compound **6** has been reported previously,[11] while **7** is new. A substance with the same molecular formula as compound **8** has been mentioned once,[12] but it was not characterized in any other way. Compound **9** has been structurally characterized by Churchill and Bird,[13] but its dynamical behavior has not been previously studied.

## Experimental Section

**Preparation of Compound 6.** A modification of the literature procedure[11] was used. A mixture of 11.1 g (105 mmol) of ω,ω-dimethylfulvene,[14] 29.0 g (148 mmol) of $Fe(CO)_5$, and 45 ml of hexane was heated in a stainless steel bomb for 9 h at 170°. After removal of solvent at reduced pressure, the resulting oil was taken up in benzene and the solution was chromatographed on alumina. Of the four bands eluted with benzene, the first three yielded only oils which could not be induced to crystallize (in accord with the previous report[11]). From the fourth band a solid was obtained on addition of petroleum ether (bp 60–110 °C) and recrystallized from benzene–petroleum ether to give 3.66 g (8% vs. the literature[11] report of 3.2%) of **6**, identified by its melting point [216–220 °C dec (lit. 200–220 °C)], its ir spectrum ($CS_2$ solution) [$\nu_{CO}$ 1995 (s), 1965 (m), 1787 (s) $cm^{-1}$ (lit. (KBr pellet) 2012 (w), 1988, 1938 (w), 1799 (w), 1767 $cm^{-1}$)], and its $^1H$ NMR spectrum ($CDCl_3$, previously unreported) [$\tau$ 4.80–4.92 (complex