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The Crystal Structure of 1,1,1-Trifluoro-5,5,5-trimethylpentanedionatocarbonyltriphenylphosphinerhodium(I)

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Introduction

The fact that only one of the carbonyl groups in complexes of the type [Rh(LL′)(CO)$_2$] (where LL′ = singly charged bidentate ligands like β-diketones, 8-hydroxyquinoline, etc.) can be substituted by triphenylphosphine [1, 2] was used to determine the relative *trans* influence of the two bonding atoms for a number of bidentate ligands [3–7] since it may be assumed that the carbonyl group *trans* to the donor atom with the largest *trans* influence in the chelate ring will be substituted by the PPh$_3$ ligand. These results were also confirmed by means of the determination of the rhodium–ligand bond distances in [Rh(TFBA)(COD)] [8] (TFBA = trifluorobenzoylacetone) and [Rh(oxine)(COD)] [9]. All the results (*vide supra*) indicated that the most electronegative atom (or in the case of β-diketones, the oxygen atom nearest to the strongest electron attracting group, like a CF$_3$-group) has the smallest *trans* influence. This is in agreement with the polarization theory [10] and the *σ-trans* effect [11].

The crystal structure determination of [Rh(TFDMAA)(CO)(PPh$_3$)] [12] (TFDMAA = 1,1,1-trifluoro-5,5-dimethylpentanedione) however indicated that substituents of the β-diketone may cause steric hindrance and may dominate the electronic effect to result in the isomer with the PPh$_3$-group *trans* to the oxygen atom nearest to the strong electron attracting CF$_3$-group. The crystal structure of [RH(TFTMAA)(CO)(PPh$_3$)], similarly prepared by means of the reaction:

$$[\mathrm{Rh(TFTMAA)(CO)_2}] + \mathrm{PPh_3} \longrightarrow [\mathrm{Rh(TFTMAA)(CO)(PPh_3)}] + \mathrm{CO}$$

has been determined to lend extra support to the above-mentioned conclusions about the *trans* influence of the donor atoms of different chelating ligands.

Experimental

[Rh(TFTMAA)(CO)(PPh$_3$)] was synthesized as described for [Rh(TFDMAA)(CO)(PPh$_3$)] [12], yield 90%. It was recrystallized from acetone. Microscopic examination of the crystals obtained, showed that only one isomer formed even up to the stage of complete evaporation of the solvent. Yellow crystals, suitable for X-ray analysis, were obtained. Crystal data: $C_{27}H_{25}O_3F_3PRh$, molecular weight 588.4, monoclinic, space group $P2_1/c$, $a = 14.991$, $b = 10.134$, $c = 18.719$ Å, $\beta = 111.19°$, $Z = 4$, μ(Mo Kα) = 7.17 cm^{-1}. The three dimensional intensity data were collected for θ values between 3 and 23° on a Philips PW1100 four circle X-ray diffractometer, using graphite monochromated Mo Kα radiation. A crystal with dimensions 0.4 × 0.4 × 0.04 mm was used for the data collection. No decomposition of the crystal was detected during the data collection. A total of 3890 independent reflections were measured of which 2508 were considered as observed. Only Lorentz and polarization corrections were applied.

The structure solution was achieved by Patterson and Fourier methods. All the non-hydrogen atoms were refined anisotropically. The final R-value was 0.063. The final atomic parameters are listed in Table I.

Discussion

The bond lengths and angles are tabulated in Table II, while the system of numbering of the atoms in the molecule is shown in Fig. 1.

The bond lengths and angles in the β-diketone and PPh$_3$ ligands compare well with those found in similar complexes of rhodium(I).

The calculation of the best plane through the coordination polyhedron showed it to be planar as expected for dsp^2 hybridization. The Rh–P bond distance (2.238 Å) is the same as in other β-diketone complexes of Rh(I) [3, 12] but significantly shorter than the Rh–P bond length *trans* to a nitrogen atom [5, 6] indicating that a nitrogen atom has a larger *trans* influence than an oxygen atom in these type of compounds.

According to the crystal structure determination the carbonyl group *trans* to the oxygen atom nearest to the electronegative CF$_3$-group has been substituted during the reaction

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TABLE I. Positional Parameters ($\times 10^4$) with Standard Deviations

Atom	*x*	*y*	*z*
Rh	2056(1)	1146(1)	2212(1)
P	1242(2)	2609(3)	1320(2)
O(1)	3206(5)	2421(7)	2534(4)
O(2)	2891(6)	−163(8)	3031(5)
O(3)	372(8)	−598(11)	1882(8)
F(1)	3940(10)	−2244(9)	3646(7)
F(2)	5116(6)	−1065(11)	4296(7)
F(3)	3898(7)	−1141(12)	4573(6)
C(1)	4187(9)	−1106(16)	3979(8)
C(2)	3744(9)	60(12)	3453(7)
C(3)	4321(8)	1155(12)	3525(7)
C(4)	4007(8)	2302(11)	3076(6)
C(5)	4664(9)	3511(13)	3226(7)
C(6)	4273(13)	4563(17)	2600(11)
C(7)	5685(11)	3134(19)	3296(12)
C(8)	4712(18)	4128(20)	4006(11)
C(9)	1039(10)	123(12)	1990(8)
C(10)	1596(9)	2614(10)	485(6)
C(11)	2546(9)	2288(15)	596(7)
C(12)	2857(10)	2286(18)	−22(8)
C(13)	2227(13)	2615(18)	−750(8)
C(14)	1269(13)	2924(17)	−865(8)
C(15)	939(10)	2881(13)	−246(6)
C(16)	−66(8)	2490(10)	912(6)
C(17)	−650(9)	3476(12)	1019(7)
C(18)	−1650(10)	3336(14)	706(9)
C(19)	−2041(10)	2220(20)	285(8)
C(20)	−1463(10)	1240(17)	170(8)
C(21)	−471(10)	1350(15)	484(7)
C(22)	1471(8)	4287(10)	1701(6)
C(23)	1430(9)	4460(12)	2430(7)
C(24)	1624(11)	5718(16)	2751(8)
C(25)	1828(11)	6796(13)	2356(9)
C(26)	1846(10)	6598(14)	1626(9)
C(27)	1676(10)	5304(12)	1295(7)

$$\mathrm{Rh(TFTMAA)(CO)_2] + PPh_3 \longrightarrow [Rh(TFTMAA)(CO)(PPh_3)] + CO}$$

This result is in contrast to which one would expect according to the polarization theory and relative *σ-trans* effect of the two oxygen atoms of the chelate ring since the oxygen atom nearest to the electron attracting CF_3-group would be the weaker electron donor. The kinetic study [13] of the substitution of the CO-groups in these type of complexes, indicated that the reaction proceeded via an associative mechanism. Square planar substitution reactions in general are thought to proceed through a trigonal bipyramidal transition state in which the entering ligand, the leaving group and the group *trans* to the leaving group, occupy the trigonal plane of the trigonal bipyramid [14]. If the expected isomer (according to the *σ-trans* effect) is to be formed

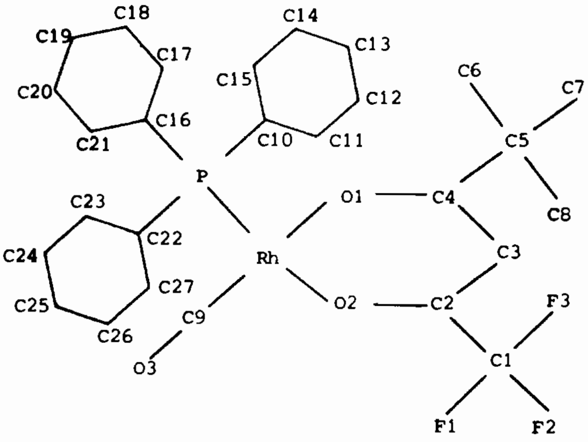

Fig. 1. The system of atom numbering in the molecule.

TABLE II. Selected Bond Lengths (Å) and Bond Angles (deg)

Rh–O(1)	2.061(7)	C(3)–C(4)	1.411(16)
Rh–O(2)	2.070(8)	C(2)–C(3)	1.383(18)
Rh–C(9)	1.765(14)	C(2)–O(2)	1.256(14)
Rh–P	2.238(3)	C(4)–C(5)	1.533(17)
O(1)–C(4)	1.266(11)	C(1)–C(2)	1.528(19)
C(9)–O(3)	1.195(14)		
C(5)–CH_3 (av.)	1.546(23)		
P–C (phenyl, av.)	1.818(12)		
C–C (phenyl, av.)	1.399(20)		
P–Rh–C(9)	91.2(4)	Rh–O(1)–C(4)	128.7(7)
P–Rh–O(1)	88.6(2)	C(2)–C(3)–C(4)	122.7(10)
O(2)–Rh–C(9)	92.2(5)	C(3)–C(4)–O(1)	124.8(10)
O(1)–Rh–O(2)	88.1(3)	C(3)–C(2)–O(2)	131.6(11)
Rh–C(9)–O(3)	176.1(12)	Rh–O(2)–C(2)	123.7(8)
Rh–P–C (phenyl, av.)	114.1(4)		
C–C–C (phenyl, av.)	120.0(14)		

during this reaction, the oxygen atom next to the bulky $C(CH_3)_3$-group, the leaving CO and incoming PPh_3 ligand, have to occupy the trigonal plane of the trigonal bipyramid. Such an intermediate would be relative unstable due to steric hindrance between these bulky groups. It is thus likely that the other isomer (via the intermediate with the PPh_3, leaving CO and oxygen atom nearest to the CF_3-group in the trigonal plane) will be formed during this reaction. The explanation that steric hindrance by bulky groups may dominate the electronic effect in determining the geometry of the reaction product will be further investigated by means of the crystal structure determination of $[Rh(TFMAA)(CO)(PPh_3)]$ and $[Rh(TFAA)(CO)PPh_3)]$, TFMAA = 1,1,1-trifluoro-5-methylpentanedione and TFAA = trifluoroacetylacetone. The trigonal bipyramidal transition state in the formation of these complexes (especially in the case of $[Rh(TFAA)(CO)(PPh_3)]$) will experience much less steric strain. It is thus expected that the specific isomer in this case will be determined by the electronic effect of the two oxygen atoms of the chelate ring rather than by steric effects.

Acknowledgements

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