The Crystal Structures of 1,1,1-Trifluoro-2,4-hexanedionatocarbonyltriphenylphosphinerhodium(I) and 1,1,1-Trifluoro-2,4-pentanedionatocarbonyltri-*p*-chlorophenylphosphinerhodium(I)

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Abstract

[Rh(TFHD)(CO)(PPh_3)] and [Rh(TFAA)(CO)(P($PhCl)_3$)] were synthesized by means of the reaction between the corresponding dicarbonyl complexes and PPh_3 and P$(PhCl)_3$, respectively. Both these compounds crystallized in the triclinic space group $P\bar{1}$ with $a = 13.651(4)$, $b = 8.941(3)$, $c = 10.642(4)$ Å, $\alpha = 96.88(3)°$, $\beta = 71.66(3)°$, $\gamma = 106.22(3)°$, $Z = 2$ and $a = 20.028(5)$, $b = 15.517(4)$, $c = 8.679(4)$ Å, $\alpha = 90.37(3)°$, $\beta = 96.58(3)°$, $\gamma = 102.59(3)°$, $Z = 4$, respectively. The numbers of observed reflections were 2351 and 5771 and the final R value 0.081 and 0.048, respectively. The carbonyl group *trans* to the oxygen atom nearest to the CF_3 group was substituted during the reaction of PPh_3, with [Rh(TFHD)$(CO)_2$] and the other way around during the reaction of [Rh(TFAA)$(CO)_2$] with P$(PhCl)_3$.

Introduction

Only one of the carbonyl groups in complexes of the type [RhLL'$(CO)_2$], where LL' is a bidentate ligand like β-diketone, 8-hydroxyquinoline and picolinic acid, can be substituted by triphenylphosphine, PPh_3 [1]. This fact was used to determine the relative *trans* influence of the two bonding atoms for a number of bidentate ligands [2–7], since it may be assumed that the carbonyl group *trans* to the donor atom with the largest *trans* influence will be substituted by the PPh_3 ligand. These results were also confirmed in a few cases by means of the determination of the rhodium–ligand bond distances *trans* to the bonding atoms of the chelate ring [8, 9]. The results, in general, indicated that the most electronegative atom (or in the case of β-diketones, the oxygen atom nearest to the strongest electron attracting substituent like CF_3 group) has, in agreement with the polarization theory [10] and the *trans* effect [11], the smallest *trans* influence.

The results of the structure determination of [Rh(TFTMAA)(CO)(PPh_3)] and [Rh(TFDMAA)(CO)(P$(PhCl)_3$)] (TFTMAA = 1,1,1-trifluoro-5,5,5-trimethylpentanedione and TFDMAA = 1,1,1-trifluoro-5,5-dimethylpentanedione), however, indicated that bulky substituents of the β-diketone may cause steric hindrance and dominate the electronic effect in the determination of the specific isomer formed during the reaction between [RhLL'$(CO)_2$] and PPh_3 [4, 5]. The crystal structures of [Rh(TFHD)(CO)(PPh_3)] and [Rh(TFAA)(CO)(P$(PhCl)_3$)] have been determined to complete a wide range of β-diketones to lend extra support to the above-mentioned conclusion about the *trans* influence of the donor atoms of different chelating ligands.

Experimental

[Rh(TFHD)(CO)(PPh_3)] (**A**) and [Rh(TFAA)(CO)(P$(PhCl)_3$)] (**B**) were synthesized as described for [Rh(TFDMAA)(CO)(PPh_3)] [5]. These compounds were recrystallized from acetone; well formed yellow crystals were obtained in both cases. The microscopic examination of the crystals of both compounds at a stage of nearly complete evaporation of the solvent, indicated that only one isomer formed during the reaction.

The crystal data and some details for the data collection and structure determination are given in Table I. No decomposition of the crystals was detected during the data collection. 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 atomic coordinates are listed in Table II. There are two crystallographic independent [Rh(TFAA)(CO)(P$(PhCl)_3$)] molecules in the triclinic unit cell which are labelled molecule 1 and molecule 2. See also 'Supplementary Material'.

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TABLE I. Crystallographic Data for [Rh(TFHD)(CO)(PPh_3)] (A) and [Rh(TFAA)(CO)(P(PhCl)$_3$)] (B)

	A	B
Formula	$C_{25}H_{21}O_3F_3PRh$	$C_{24}H_{16}O_3F_3Cl_3PRh$
Molecular mass	560.32	649.62
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.651(4)	20.028(5)
b (Å)	8.941(3)	15.517(4)
c (Å)	10.642(4)	8.679(4)
α (°)	96.88(3)	90.37(3)
β (°)	71.66(3)	96.58(3)
γ (°)	106.22(3)	102.59(3)
V (Å^3)	1183.1	2613.7
Z	2	4
D_{exp} (g cm^{-3})	1.553	1.583
Crystal dimensions (mm)	0.2 × 0.15 × 0.1	0.24 × 0.16 × 0.1
θ limits	$3 < \theta < 23$	$3 < \theta < 23$
Unique reflections	3270	7267
Observed reflections	2351	5771
Radiation	Mo Kα	Mo Kα
μ(Mo Kα)	8.13	10.05
R	0.081	0.048

TABLE II. Fractional Atomic Coordinates (×10^4) (e.s.d.s in parentheses)

Atom	Rh(TFHD)(CO)(PPh_3)			Rh(TFAA)(CO)(P(PhCl)$_3$)					
	x	y	z	Molecule 1			Molecule 2		
				x	y	z	x	y	z
Rh	2534(0)	1896(0)	4970(0)	2629(0)	3592(0)	1076(1)	7319(0)	1362(0)	7354(1)
P	3543(3)	1105(4)	3028(3)	2277(1)	4062(1)	3214(2)	7383(1)	901(1)	9681(2)
C(1)	3573(11)	1918(16)	5675(14)	2076(6)	4147(6)	−136(10)	7836(6)	771(7)	6411(10)
O(1)	4231(11)	1952(17)	6128(12)	1737(5)	4498(6)	−965(8)	8140(5)	397(7)	5717(8)
O(2)	1577(8)	2538(12)	6802(10)	3256(3)	2947(4)	2426(6)	6714(3)	2038(4)	8386(6)
O(3)	1353(8)	1945(13)	4187(11)	2979(3)	3146(4)	−870(6)	6967(3)	1809(4)	5230(6)
F(1)	−730(14)	3296(28)	8798(17)	4511(4)	1718(5)	2747(1)	5499(4)	3334(5)	8055(7)
F(2)	−96(14)	1716(21)	9246(14)	4357(3)	2673(4)	4335(6)	5629(3)	2368(4)	9701(7)
F(3)	783(12)	3944(20)	9108(15)	3596(4)	1490(5)	3850(8)	6414(4)	3520(5)	9659(8)
C(2)	155(14)	3022(27)	8506(23)	4041(5)	2099(6)	3198(11)	5959(5)	2933(7)	8747(10)
C(3)	644(13)	2686(18)	7060(17)	3665(4)	2540(5)	1925(9)	6321(4)	2475(5)	7669(9)
C(4)	69(14)	2543(22)	6173(20)	3802(4)	2426(6)	424(10)	6184(4)	2598(5)	6109(9)
C(5)	437(15)	2217(23)	4798(22)	3445(4)	2724(5)	−889(9)	6526(4)	2262(5)	4965(9)
C(6)	−317(19)	1693(44)	3540(41)	3634(6)	2523(8)	−2496(10)	6354(6)	2483(8)	3268(10)
C(7)	−52(40)	3146(37)	3218(48)						
C(8)	3328(10)	1673(14)	1555(12)	1766(4)	4894(5)	2926(9)	8197(4)	68(5)	9712(8)
C(9)	4159(11)	2615(16)	631(13)	1085(5)	4622(6)	2206(10)	7961(4)	−778(5)	10248(10)
C(10)	3941(13)	3055(17)	−467(15)	690(5)	5252(8)	1813(10)	8358(5)	−1416(6)	10178(12)
C(11)	2943(15)	2587(19)	−629(16)	1007(6)	6140(8)	2154(12)	8975(4)	−1185(6)	9519(10)
C(12)	2063(13)	1558(20)	319(16)	1659(6)	6412(6)	2885(14)	9223(4)	−347(6)	8979(9)
C(13)	2305(11)	1142(16)	1418(15)	2057(4)	5793(5)	3285(12)	8829(4)	284(5)	9096(9)
C(14)	4990(9)	1865(14)	2739(12)	3003(4)	4553(4)	4645(8)	6956(4)	418(5)	10718(8)
C(15)	5386(11)	3414(15)	3084(14)	3626(4)	4916(5)	4117(10)	7011(5)	436(5)	12334(9)
C(16)	6485(12)	4025(16)	2849(15)	4203(4)	5286(5)	5184(11)	6450(5)	76(6)	13093(10)
C(17)	7175(13)	3042(21)	2313(17)	4132(5)	5269(5)	6766(10)	5842(4)	−292(5)	12218(11)
C(18)	6784(11)	1527(22)	1996(17)	3570(5)	4917(6)	7312(10)	5767(4)	−335(5)	10697(10)
C(19)	5668(11)	923(16)	2209(14)	2943(5)	4564(5)	6238(9)	6335(4)	38(5)	9846(10)

(continued)

TABLE II. *(continued)*

Atom	Rh(TFHD)(CO)(PPh$_3$)			Rh(TFAA)(CO)(P(PhCl)$_3$)					
				Molecule 1			Molecule 2		
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C(20)	3287(9)	–1019(13)	2861(13)	1745(4)	3193(5)	4243(8)	8206(4)	1783(5)	10990(8)
C(21)	3215(11)	–1806(15)	1642(15)	1263(4)	3379(6)	5151(9)	8044(5)	2614(5)	10899(10)
C(22)	3032(12)	–3438(16)	1560(17)	848(5)	2702(6)	5854(10)	8429(5)	3307(6)	11871(10)
C(23)	2914(12)	–4270(17)	2640(19)	930(5)	1847(6)	5628(10)	8959(5)	3148(6)	12912(9)
C(24)	2998(13)	–3466(17)	3826(17)	1414(6)	1648(6)	4774(10)	9119(5)	2330(7)	13048(11)
C(25)	3186(12)	–1856(16)	3944(15)	1830(5)	2334(6)	4062(9)	8739(5)	1643(6)	12064(10)
Cl(1)				522(2)	6927(2)	1637(5)	9461(1)	–1978(2)	9414(4)
Cl(2)				4849(1)	5701(2)	8084(3)	5124(1)	–732(2)	13168(3)
Cl(3)				366(2)	981(2)	6396(4)	9451(1)	4034(2)	14096(3)

TABLE III. Selected Interatomic Distances (Å) (e.s.d.s in parentheses)

	Rh(TFHD)(CO)(PPh$_3$)	Rh(TFAA)(CO)(P(PhCl)$_3$)	
		Molecule 1	Molecule 2
Rh–C(1)	1.796(17)	1.797(11)	1.783(12)
Rh–P	2.252(3)	2.231(2)	2.243(2)
Rh–O(2)	2.094(9)	2.045(6)	2.039(6)
Rh–O(3)	2.048(13)	2.071(6)	2.075(5)
O(2)–O(3)	1.258(21)	1.250(11)	1.263(10)
C(3)–C(4)	1.380(31)	1.380(12)	1.374(11)
C(4)–C(5)	1.412(29)	1.410(12)	1.426(13)
O(3)–C(5)	1.290(22)	1.254(11)	1.246(11)
C(1)–O(1)	1.137(24)	1.153(14)	1.142(16)
C(3)–C(2)	1.503(27)	1.516(13)	1.508(14)
C(5)–C(6)	1.876(48)	1.533(13)	1.532(12)
C(6)–C(7)	1.305(53)		
C(2)–F(1)	1.237(30)	1.309(14)	1.314(13)
C(2)–F(2)	1.388(31)	1.329(11)	1.331(12)
C(2)–F(3)	1.284(27)	1.328(12)	1.322(11)
P–C(8)	1.835(15)	1.816(9)	1.818(9)
P–C(14)	1.837(12)	1.824(7)	1.823(8)
P–C(20)	1.830(12)	1.833(7)	1.829(7)
C(11)–Cl(1)		1.749(13)	1.736(11)
C(17)–Cl(2)		1.736(9)	1.751(10)
C(23)–Cl(3)		1.747(9)	1.753(8)

Results and Discussion

The bond lengths and angles are given in Tables III and IV, respectively, while the systems of numbering of the atoms in the molecules, are shown in Figs. 1 and 2. All the bond lengths and angles compare well with those found in similar complexes of rhodium(I) [2–5].

The crystal structure determination of [Rh(TFAA)(CO)(P(PhCl)$_3$)] showed that the carbonyl group *trans* to the oxygen atom nearest to the electronegative CF$_3$ group was not substituted during the reaction

$$[\mathrm{Rh(TFAA)(CO)_2}] + \mathrm{P(PhCl)_3} \longrightarrow [\mathrm{Rh(TFAA)(CO)(P(PhCl)_3)}] + \mathrm{CO}$$

This result is in agreement with the polarization theory and the expected *trans* influence of the two oxygen atoms of the chelate ring, since the oxygen atom nearest to the electron attracting CF$_3$ group would be less polarizable and a weaker electron donor. The structures of [Rh(TFHD)(CO)(PPh$_3$)],

TABLE IV. Selected Bond Angles (°) (e.s.d.s in parentheses)

	$\mathrm{Rh(TFHD)(CO)(PPh_3)}$	$\mathrm{Rh(TFAA)(CO)(P(PhCl)_3)}$	
		Molecule 1	Molecule 2
C(1)–Rh–O(3)	178.1(6)	90.3(4)	90.1(3)
C(1)–Rh–O(2)	91.4(5)	179.1(3)	178.7(2)
O(2)–Rh–O(3)	87.5(4)	88.9(2)	88.6(2)
O(2)–Rh–P	177.7(3)	89.5(2)	89.8(2)
O(3)–Rh–P	92.9(3)	178.3(2)	178.5(2)
P–Rh–C(1)	88.1(4)	91.3(3)	91.4(3)
Rh–C(1)–O(1)	179.1(14)	177.1(10)	175.5(8)
Rh–O(2)–C(3)	127.0(11)	124.8(5)	124.6(5)
O(2)–C(3)–C(4)	126.7(15)	129.7(8)	130.5(8)
C(3)–C(4)–C(5)	125.6(18)	123.8(9)	123.1(8)
C(4)–C(5)–O(3)	124.9(22)	125.7(8)	125.3(7)
C(5)–O(3)–Rh	128.1(14)	126.7(5)	127.7(5)
Rh–P–C(14)	114.7(4)	111.6(3)	110.9(2)
C(10)–C(11)–Cl(1)		117.3(11)	118.1(7)
C(16)–C(17)–Cl(2)		118.8(6)	118.6(7)
C(22)–C(23)–Cl(3)		118.5(8)	118.1(7)

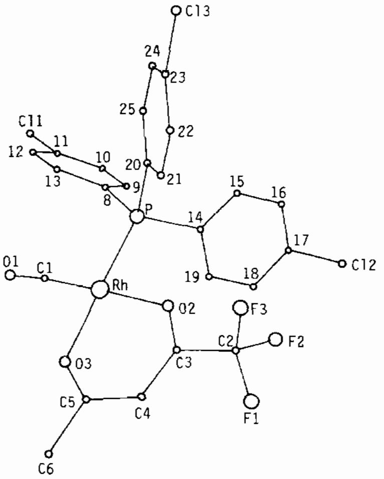

Fig. 1. Perspective view of $[\mathrm{Rh(TFAA)(CO)(P(PhCl)_3)}]$ with atom numbering scheme.

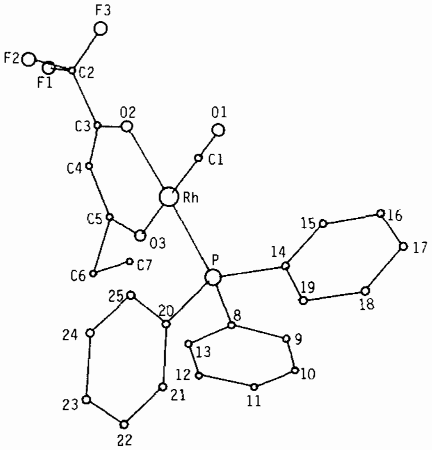

Fig. 2. Perspective view of $[\mathrm{Rh(TFHD)(CO)(PPh_3)}]$ with atom numbering scheme.

$[\mathrm{Rh(TFDMAA)(CO)(PPh_3)}]$ [5] and $[\mathrm{Rh(TFTMAA)(CO)(PPh_3)}]$ [4], however, showed that the carbonyl group *trans* to the oxygen nearest to the electronegative $\mathrm{CF_3}$ group has been substituted during the reaction

$$[\mathrm{Rh}(\beta\text{-diketone})(\mathrm{CO})_2] + \mathrm{PPh_3} \longrightarrow [\mathrm{Rh}(\beta\text{-diketone})(\mathrm{CO})(\mathrm{PPh_3})] + \mathrm{CO}$$

In the attempt to explain these results, one must keep in mind that there is a steady increase in the bulkiness of the other substituent of the β-diketone from TFAA ($-\mathrm{CH_3}$) to TFHD ($-\mathrm{CH_2CH_3}$), TFDMAA ($-\mathrm{CH(CH_3)_2}$) and TFTMAA ($-\mathrm{C(CH_3)_3}$). The kinetic study of the substitution reactions of these types of complexes indicated that these substitution reactions proceeded via an associative mechanism [12]. Such associative substitution reactions, in general, are believed to proceed via a trigonal bipyrimidal 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 [11]. If the expected isomers (according to the relative *trans* influence of the oxygen atoms of the β-diketones) are to be formed during the substitution reaction, the oxygen atom next to the bulky groups ($-\mathrm{CH_2CH_3}$, $-\mathrm{CH(CH_3)_2}$ or $-\mathrm{C(CH_3)_3}$), the leaving CO group and the incoming $\mathrm{PPh_3}$ ligand, have to occupy the trigonal plane of the trigonal bipyramid in the transition state. Such an intermediate would be relative unstable, due to the steric hindrance between these bulky groups. It is thus likely that the other isomer (via the intermediate with the $\mathrm{PPh_3}$, CO and oxygen atom next to the CF_3 group in the trigonal plane) will be formed during these reactions.

Evidence for the explanation that steric hindrance by bulky substituents on the β-diketone may dominate the electronic effect cause by strong electron withdrawing groups (like CF_3 group) in determining the specific isomer that will be formed during these substitution reactions, is found in the fact that the expected isomer (as prescribed by the relative *trans* influence of the oxygen atoms) is formed only in the case of TFAA with the relative small CH_3 group as a substituent.

Supplementary Material

Listings of the anisotropic thermal parameters, as well as the observed and calculated structure factors, may be obtained from the authors.

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