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Organometallic Lewis Acids LXIII [1]

Structure of the the chiral complex [(acetone)(carbonyl)(η^5-cyclopentadieny)(triphenylphosphine)ruthenium-tetrafluoroborate], $[(\eta^5\text{-}C_5H_5)Ru(CO)(PPh_3)(\eta^1\text{-}O{=}CMe_2)]^+BF_4^-$

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Dedicated to Professor Thomas Klapötke on the occasion of his 60th birthday

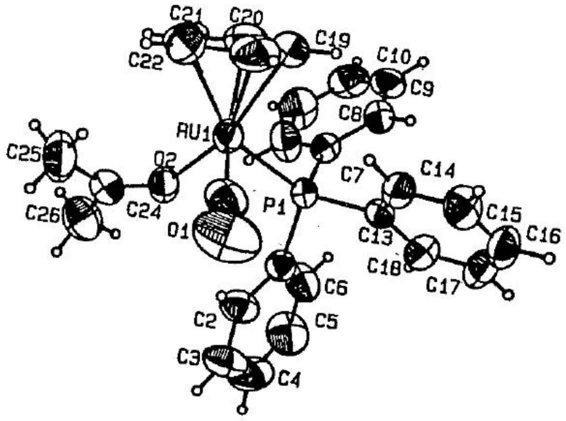
Abstract

The structure of the title complex has been determined by X ray diffraction and exhibits interesting comparison with that of the isoelectronic and isosteric Rhenium complex $[CpRe(NO)(PPh_3)(acetone)]^+BF_4^-$

Keywords: Chiral complexes; ruthenium, rhenium; acetone, carbonyl, nitrosyl.

The chiral pseudotetrahedral complexes [CpM(CO)(PPh$_3$)(X) (M = Fe, Ru) [1 - 4] and [CpRe(NO)(PPh$_3$)(X) [5] with four different ligands at the metal atom have attracted much attention as inorganic counter parts of chiral methane derivatives. The two enantiomers of these complexes could be separated]6, 7).

The title complex was synthesized by the reaction of the in situ formed Lewis acid [CpRu(CO)(PPh$_3$)]$^+$ (from [CpRu(CO)(PPh$_3$)Cl and AgBF$_4$) with acetone [2]. Crystals were obtained from dichloromethane/*n*-pentane solution.The molecular structure of the title complex, which was found as S$_{Ru}$ enantiomer in the crystal, is shown in the figure.



For the title complex the following (plausible) Ru-ligand bond lengths were found: Ru-C 1,836(5) Å, Ru-O 2.140(3) Å and Ru–P 2.320(1) Å.

Of interest is the comparison of the structure of the cationic acetone complex [CpRu(CO)(PPh$_3$)(acetone)]$^+$BF$_4^-$ with that of the Gladysz complex [CpRe(NO)(PPh$_3$)(acetone)]$^+$ BF$_4^-$ [7].The two cationic halfsandwich complexes are isoelectronic and show similar geometry with bond angles P-Ru-O = 84.5(7) °, P-Ru-C = 91.7(2)°, Ru-O-C = 134° and P-Re-O = 84.1(1)°, P-Re-N = 92.6(2)°, Re-O-C = 136.3(4)°. In the Rhenium complex the O=C acetone bond was found to be longer [1.248(9) Å] [7] as that in the Ruthenium compound [1.206(5) Å]. This difference of the O-coordinated carbonyl bonds, which is also detected in the IR frequencies of the carbonyl groups (Re: 1618 cm^{-1}, KBr ; Ru : 1645 cm^{-1}, KBr) is certainly due to the stronger Lewis acidity of the Rhenium complex, caused by the stronger π-acceptor NO in comparison to the CO ligand.

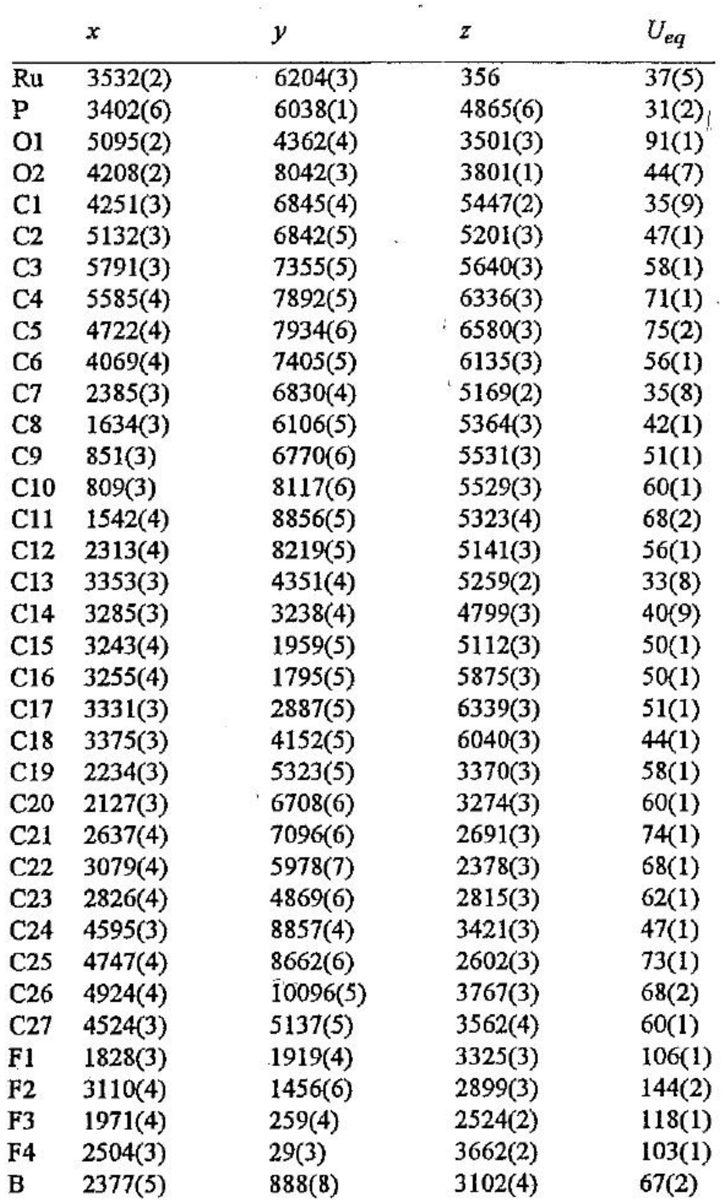
Experimental

The experimental details for the synthesis of the title complex are described in reference [2].

Table 1. Crystallographic data for $[CpRu(CO)(PPh_3)(acetone)]^+BF_4^-$

Fornula	$C_{27}H_{26}BF_4O_2PRu$
M_r	601.36
Crystal size mm^3	0.10 x 23 x 0.53
Crystal habit	orange needles
Crystal system	orthorhombic
Space group	$Pca2_1$
a, pm	1509.8
b, pm	997.6
c, pm	1770.8
V, nm 3	2.6672
Z	4
Calculated density, g cm^{-3}	1.497
Diffractomete , scan mode	Enraf Nonius CAD4, ω
μ(MoK α), cm^{-1}	6.834
T, K	296
2Θ range, deg	4 - 44
Refl. measured	3541
Refl. with $I > 3\sigma$	2869
Parameters refined	299
Program	SIR, MOLEN
R	0.0254
R_w ($w = 1/\sigma^2(F)$)	0.0339
Large diff. peak / hole, e $Å^{-3}$	1.181 / -0.192

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($x10^3$) [$Å^2$]. Equivalent isotropic U calculated as one third of the "Spur" of the orthogonal U_{ij} tensor



	x	y	z	U_{eq}
Ru	3532(2)	6204(3)	356	37(5)
P	3402(6)	6038(1)	4865(6)	31(2)
O1	5095(2)	4362(4)	3501(3)	91(1)
O2	4208(2)	8042(3)	3801(1)	44(7)
C1	4251(3)	6845(4)	5447(2)	35(9)
C2	5132(3)	6842(5)	5201(3)	47(1)
C3	5791(3)	7355(5)	5640(3)	58(1)
C4	5585(4)	7892(5)	6336(3)	71(1)
C5	4722(4)	7934(6)	6580(3)	75(2)
C6	4069(4)	7405(5)	6135(3)	56(1)
C7	2385(3)	6830(4)	5169(2)	35(8)
C8	1634(3)	6106(5)	5364(3)	42(1)
C9	851(3)	6770(6)	5531(3)	51(1)
C10	809(3)	8117(6)	5529(3)	60(1)
C11	1542(4)	8856(5)	5323(4)	68(2)
C12	2313(4)	8219(5)	5141(3)	56(1)
C13	3353(3)	4351(4)	5259(2)	33(8)
C14	3285(3)	3238(4)	4799(3)	40(9)
C15	3243(4)	1959(5)	5112(3)	50(1)
C16	3255(4)	1795(5)	5875(3)	50(1)
C17	3331(3)	2887(5)	6339(3)	51(1)
C18	3375(3)	4152(5)	6040(3)	44(1)
C19	2234(3)	5323(5)	3370(3)	58(1)
C20	2127(3)	6708(6)	3274(3)	60(1)
C21	2637(4)	7096(6)	2691(3)	74(1)
C22	3079(4)	5978(7)	2378(3)	68(1)
C23	2826(4)	4869(6)	2815(3)	62(1)
C24	4595(3)	8857(4)	3421(3)	47(1)
C25	4747(4)	8662(6)	2602(3)	73(1)
C26	4924(4)	10096(5)	3767(3)	68(2)
C27	4524(3)	5137(5)	3562(4)	60(1)
F1	1828(3)	1919(4)	3325(3)	106(1)
F2	3110(4)	1456(6)	2899(3)	144(2)
F3	1971(4)	259(4)	2524(2)	118(1)
F4	2504(3)	29(3)	3662(2)	103(1)
B	2377(5)	888(8)	3102(4)	67(2)

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