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Trans Effect in β-Diketone Complexes of Rhodium(I)

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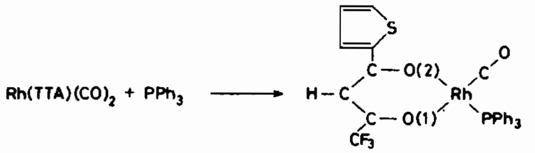
It is well known that the carbonyl groups in compounds of the type [Rh(β-diketone)(CO)$_2$] can be substituted by olefines and partially substituted by triphenylphosphine and -arsine [1]. The two carbonyl groups in symmetrical β-diketones are chemically equivalent. In the case of non-symmetrical β-diketones it is however necessary to have a knowledge about the relative reactivities of the two carbonyl groups and thus of the relative *trans* effects of the two oxygen atoms of the β-diketone. This paper deals with the *trans* effect in complexes of the type [Rh(β-diketone)(CO)$_2$] and [Rh(β-diketone)(CO)(PPh$_3$)].

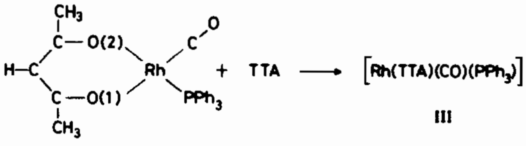
The crystal structure determination of [Rh(TTA)(CO)(PPh$_3$)], I, prepared by the reaction between [Rh(TTA)(CO)$_2$] and triphenylphosphine, PPh$_3$ [1], showed that the carbonyl group *trans* to the oxygen atom nearest to the thenoyl group has been displaced [2] (TTA = thenoyltrifluoroacetone). According to this result O(2), in I, has a larger *trans* effect than O(1). This is in agreement with the polarization theory [3] since the oxygen atom nearest to the CF$_3$-group will be least polarizable as a result of the electron-attracting power of the CF$_3$-group.



(1)

I

In the recent crystal structure determination [4] of [Rh(acac)(CO)(PPh$_3$)], II, prepared in the same way as I, the following Rh–O bond distances were found: Rh–O(2) = 2.087(4)Å and Rh–O(1) = 2.029(5)Å. The effect of the PPh$_3$-group is also observed in comparing the Rh–O bond distances in II and in [Rh(acac)(CO)$_2$] [5]. In the latter complex where the two Rh–O bonds should be equivalent the Rh–O bond distances are the same within the experimental error *i.e.* 2.040(4)Å and 2.044(4)Å. The significant difference in the two Rh–O bond distances in II indicates that the PPh$_3$-group has a larger *trans* effect than the CO-group in this type of compounds.



(2)

III

II

The Rh–C bond distances in I and II are 1.780(12)Å and 1.801(8)Å respectively. Although this difference is only about twice the standard deviation it indicates that the oxygen atom nearest the CH$_3$-group has a larger *trans* effect than the oxygen atom nearest to the CF$_3$-group. This is in agreement with the relative polarizability of the two oxygen atoms due to the electron-attracting power of the CF$_3$-group.

These results with respect to the relative *trans* effects of the different ligands can be verified according to reaction (2). The specific isomer which would be obtained according to reaction (2) would depend on (i) which Rh–O bond in II will break first, thus the relative *trans* effect of PPh$_3$ and CO and (ii) which of the two oxygen atoms of the TTA-group will bond first. According to the discussion in paragraph 3, the Rh–O(2) bond (*trans* to the PPh$_3$-group) which is the weakest of the two Rh–O bonds in II will break the first. According to the conclusion in paragraph 2, the oxygen atom nearest to the thenoyl group (which has the largest *trans* effect) will bond first since, as is well known, a good *trans* labilizer is also a good entering group in square planar substitution. Thus III should be the same isomer as I. This was verified as follows by reaction (2): 0.4 g TTA (an excess) was added to 0.2 g of II in acetone. The solution was evaporated and chromatographed on an alumina column to remove the excess TTA. The resulting product was recrystallized from acetone. The X-ray powder patterns of I and III were identical which showed that I and III was the same isomer. This experimental result thus confirms the proposals based on the structure determinations.

Acknowledgements

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