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Preliminary Communication

DIHAPTO-ACYL DERIVATIVES OF RUTHENIUM(II). PREPARATION AND STRUCTURE OF $Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2$ AND $Ru[\eta^2\text{-}C(O)p\text{-tolyl}]I(CO)(PPh_3)_2$

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SUMMARY

Reaction between $Ru(CO)_2(PPh_3)_3$ and MeHgI yields $Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2$ which in solution exists mainly as $RuCH_3I(CO)_2(PPh_3)_2$ and crystal structure determination of $Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2$ and previously described $Ru[\eta^2\text{-}C(O)p\text{-tolyl}]I(CO)(PPh_3)_2$ confirms that in the solid state both molecules contain *dihapto*-acyl ligands.

Crystal structure analyses of $Ti[\eta^2\text{-}C(O)CH_3]Cl(C_5H_5)_2$[1], $Zr[\eta^2\text{-}C(O)CH_3]CH_3(C_5H_5)_2$[2], $V[\eta^2\text{-}C(O)C_3Ph_3H_2](CO)_3(Ph_2PCH_2CH_2AsPh_2)$[3] and $[Mo[\eta^2\text{-}C(O)CH_2Si(CH_3)_3]Cl(CO)_2PMe_3]_2$[4] have demonstrated the presence of *dihapto*-acetyl ligands in these Group IV, V, and VI transition metal derivatives. Also, the chemistry of other zirconium acetyl derivatives has been rationalized on the basis of an oxy-carbenoid reactivity imparted to the carbonyl carbon as a result of the η^2-coordination mode.[5]

We have previously suggested[6] that solutions of the ruthenium compounds $RuRX(CO)_2(PPh_3)_2$, (R = *p*-tolyl; X = Cl,Br,I) were in equilibrium with $Ru[\eta^2\text{-}C(O)R]X(CO)(PPh_3)_2$ and for X = I the crystalline material also had properties consistent with a *dihapto*-acyl ligand. To confirm this suggestion we now describe crystal structure analysis of $Ru[\eta^2\text{-}C(O)R]I(CO)(PPh_3)_2$(I) and for comparison the related acetyl $Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2$(II).

Compound II was prepared by reaction of $Ru(CO)_2(PPh_3)_3$[7] with CH_3HgI in benzene. Reaction was rapid, Hg was deposited, and $Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2$ resulted in greater than 90% yield.

$$Ru(CO)_2(PPh_3)_3 + CH_3HgI \longrightarrow Ru[\eta^2\text{-}C(O)CH_3]I(CO)(PPh_3)_2 + Hg\downarrow + PPh_3$$

Solutions of II exist substantially in the dicarbonyl form *viz.*,

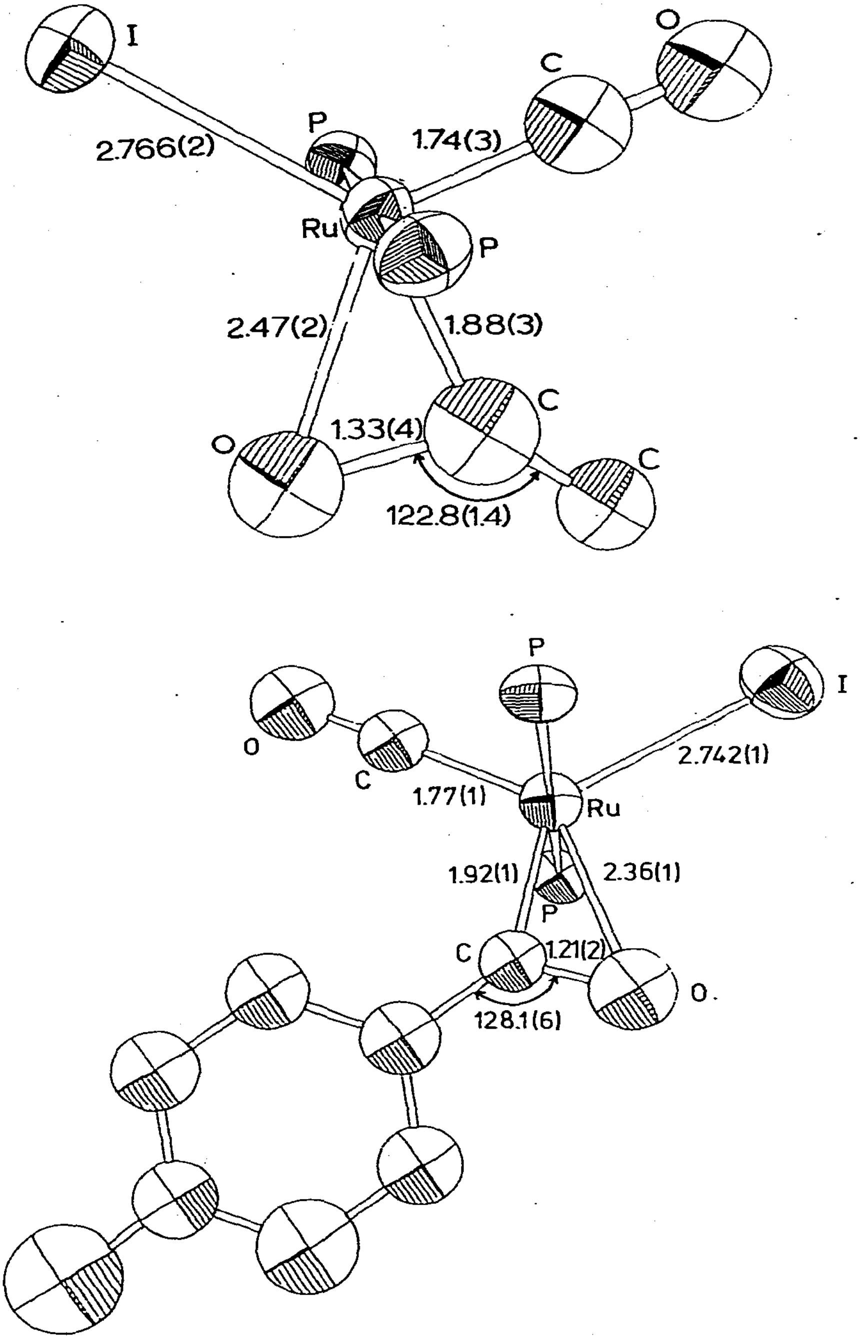

Figure. Coordination geometry of Ru[η^2-C(O)*p*-tolyl]I(CO)(PPh$_3$)$_2$ and Ru[η^2-C(O)CH$_3$]I(CO)(PPh$_3$)$_2$

$RuCH_3I(CO)_2(PPh_3)_2$, ν_{CO} in CH_2Cl_2 at 2025 and 1966 cm^{-1} and the ^1H N.M.R. spectrum in $CDCl_3$ shows a triplet at τ, 9.11 (CH_3, J_{p-H} 2.2 Hz). However, crystalline II shows only one terminal ν_{CO} at 1907 cm^{-1} and in addition a band in the region appropriate for an η^2-acetyl at 1599 cm^{-1}.

Compounds I and II both crystallize in the triclinic system (space group $P\bar{1}$) with z = 2. Unit cell dimensions for compound I are a = 13.394(1), b = 13.668(1), c = 12.220(1)Å, α = 116.01(1), β = 105.48(1), γ = 81.44(1)°, those for II are a = 12.273(1), b = 13.817(1), c = 11.640(1)Å, α = 97.67(1), β = 101.27(1), γ = 64.99(1)°. Intensity data were collected on a Hilger-Watts four-circle diffractometer. Compound I showed decomposition both with time and in the X-ray beam (CuK_α radiation) and a total of 1919 unique reflections with $I > 5\sigma(I)$ were recorded from two crystals (θ_{max} = 51°). A change to MoK_α radiation was made for II but again only limited data were recorded from two crystals (1208 unique reflections for which $I > 3\sigma(I)$°, θ_{max} = 15°). The structures were solved by Patterson and Fourier methods and have been refined to R's of 0.068 and 0.040 for I and II respectively. The figure shows the coordination geometry of both molecules with the acyl group bound as a *dihapto* ligand in each. This group is attached in an asymmetric manner with the Ru-C distance being much shorter than that for Ru-O. The mean $[\text{Ru-O}_{distance} - \text{Ru-C}_{distance}]$ is 0.52 Å and this may be compared with the corresponding $[\text{M-O}_{distance} - \text{M-C}_{distance}]$ for the Zr, V, and Mo compounds which is respectively 0.09 A, 0.23 Å, and 0.27 Å. It is clear that the *dihapto*-character is less pronounced for the ruthenium compounds and this may be associated with the reverse migration reaction to form the alkyl-dicarbonyl compounds which occurs so readily in solution.

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