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Preliminary communication

PREPARATION AND STRUCTURE OF THE SECONDARY CARBENE COMPLEX $\mathrm{RuI_2[CHN(CH_3)(\mathit{p}\text{-}CH_3C_6H_4)](CO)(CN\text{-}\mathit{p}\text{-}CH_3C_6H_4)(PPh_3)}$

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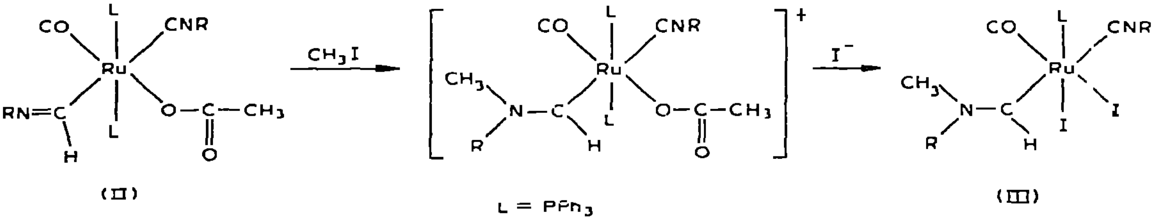
Summary

Crystal structure determination of the complex $\mathrm{RuI_2[CHN(CH_3)(\mathit{p}\ CH_3C_6H_4)]}$ $\mathrm{(CO)(CN\ \mathit{p}\text{-}CH_3C_6H_4)(PPh_3)}$ reveals a short C—N bond within the carbene ligand (1.28 Å), a large RuCN angle (139°), and permits internal comparison of the bond lengths Ru—C(carbene), Ru—C(isocyanide) and Ru—C(carbonyl).

Various compounds containing the secondary carbenes CHNHR and $\mathrm{CHN(CH_3)R}$, (R = *p* tolyl) result from modification of the formimidoyl group in $\mathrm{Ru(O_2CCH_3)(CHNR)(CO)(PPh_3)_2}$ (I) [1]. When the chelating acetate ligand in I is opened by CNR, $\mathrm{Ru(OCOCH_3)(CHNR)(CO)(CNR)(PPh_3)_2}$ (II) results. II has ν(CO), 1970vs $\mathrm{cm^{-1}}$, ν(CN) 2100s $\mathrm{cm^{-1}}$ (CNR) and ν(CN), 1540s $\mathrm{cm^{-1}}$ (formimidoyl). The formimidoyl group in II is readily methylated by $\mathrm{CH_3I}$ and iodide replaces both acetate and triphenylphosphine to produce the neutral secondary carbene complex $\mathrm{RuI_2(CHN(CH_3)R)(CO)(CNR)(PPh_3)}$ (III) (ν(CO), 1975s $\mathrm{cm^{-1}}$, ν(CN), 2160s $\mathrm{cm^{-1}}$ (CNR) and ν(CN), 1520s $\mathrm{cm^{-1}}$ (carbene))



Replacement of phosphine by iodide in a bis-phosphine octahedral complex of a d^6 platinum metal is unusual but has been observed with an iridium (III) complex which, significantly, also contained a carbene ligand [2]. Compound III is ideally suited for crystal structure investigation, to provide details of the geometry of the $\mathrm{CHN(CH_3)R}$ carbene ligand which can be compared with the known structure of its formimidoyl precursor [3], and also to provide an internal comparison of Ru—C(carbene), Ru—C(isocyanide) and Ru—C(carbonyl).

Compound III crystallizes in the triclinic space group $P\bar{1}$, with a = 11.640(1) b = 10.9139(8), c = 16.587(2) Å, α 87°59′, β 99°40′, γ 62°15′, Z = 2. Intensity data were collected on a Hilger and Watts automatic diffractometer with Mo-K_α X-radiation. The structure was solved using standard Patterson and Fourier syntheses and is being refined by least-squares methods At present only the ruthenium and iodine atoms have been assigned anisotropic thermal parameters, the conventional R-factor is 0 055 for 2731 "observed" reflections.

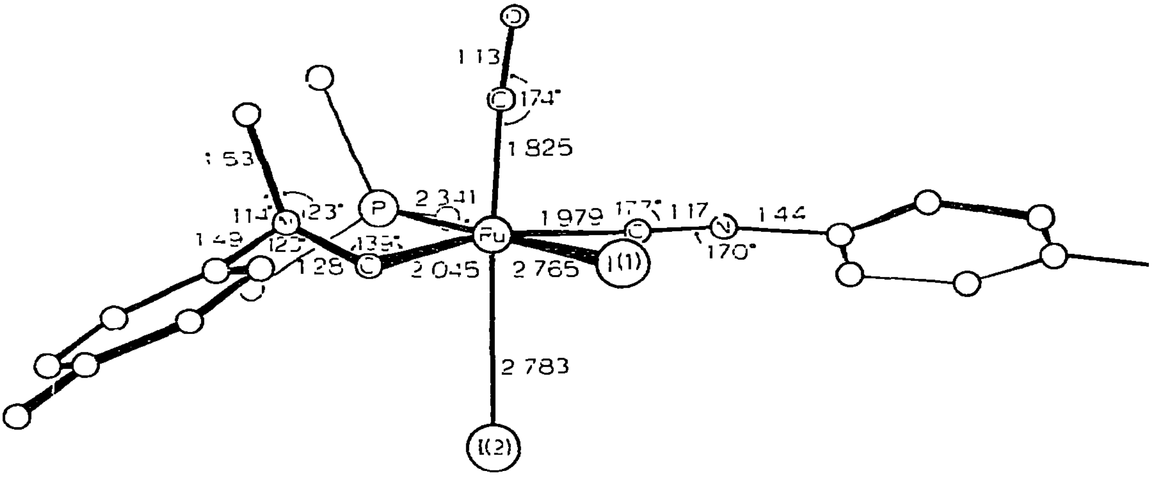


Fig 1 Bond lengths (Å) and angles in $RuI_2(CHN(CH_3)R)(CO)(CNR)(PPh_3)$

The structure is shown in Fig. 1. The geometry suggested in the above scheme is verified with the iodine atoms mutually *cis* and the carbene and isocyanide ligands *trans* to one another. The coordination octahedron is not regular with the carbene carbon, C(9), being the most displaced from its ideal position (I(1)—Ru—C(9), 80.9°, P—Ru—C(9), 98.2°; C(isocyanide)—Ru—C(9). 164.7°). The C—N bond distance of 1 28 Å is noticeably shorter than the distances found, (1.31-1.38 Å) in other carbene complexes [4] but is lengthened with respect to the bond length found in $Ru(O_2CCH_3)(CHNR)(CO)(PPh_3)_2$ [3] The Ru—C (carbene) bond is only slightly longer than in the formimidoyl precursor, comparable with Ru—C(isocyanide), but longer than Ru—C(carbonyl) (see Fig. 1). The Ru—C bond in an octahedral Ru^{II} imidazol-ylidine complex at 2.128(4) Å [5] is longer than the Ru—C (secondary carbene) distance found here and despite the very short C—N bond there must be some multiple bond character in the Ru—carbene bond.

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