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Preliminary communication

CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY. SYNTHESES AND DEPROTONATION OF SOME VINYLIDENE-RUTHENIUM COMPLEXES.

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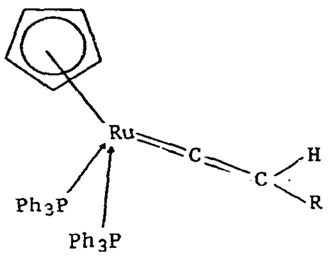
Summary. Reactions between 1-alkynes and $RuCl(PPh_3)_2(\eta-C_5H_5)$ in the presence of NH_4PF_6 afford the cationic vinylidene complexes $[Ru(C{:}CHR)(PPh_3)_2(\eta-C_5H_5)]PF_6$; these are readily deprotonated by base to give the η^1-alkynyl derivatives $Ru(C{\equiv}CR)(PPh_3)_2(\eta-C_5H_5)$. The latter may be protonated to reform the monosubstituted vinylidene complexes.

Recent publications have described the isolation and characterisation of dicyanovinylidene complexes of molybdenum[1], and of phenylvinylidene complexes of manganese[2,3] and rhenium[4]. The latter were obtained in low yield from $M(CO)_3(\eta-C_5H_5)$ (M = Mn or Re) and phenylacetylene in tetrahydrofuran. Others have implicated similar complexes of platinum, $Pt\overset{+}{C}{=}CHR$, as intermediates in the formation of the methoxycarbene complexes *trans*-$PtMe[C(OMe)CH_2R]L_2$ ($L = PMe_2Ph, AsMe_3$) from reactions between 1-alkynes and *trans*-$PtClMeL_2$ in methanol in the presence of $AgPF_6$,[5] and of ruthenium in the dimerisation of *t*-butylacetylene to 1,4-di-*t*-butylbuta-1,2,3-triene by $RuH_2(CO)(PPh_3)_3$.[6] The reaction between phenylacetylene and *trans*-$FeCl_2(depe)_2$ [depe = $Et_2P(CH_2)_2PEt_2$] affords a complex thought to contain the C:CHPh ligand on the basis of IR, ^1H NMR and Mössbauer spectrometry.[7] Herein we describe a simple, high yield synthesis of some cationic vinylidene complexes of ruthenium, their characterisation, and conversion into σ-alkynyl derivatives.

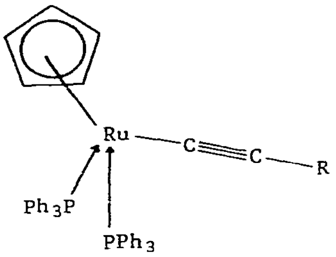
The reactions of $RuCl(PPh_3)_2(\eta-C_5H_5)$[8] with 1-alkynes in methanol, in the presence of NH_4PF_6 (or $NaBPh_4$) give pale red-purple compounds of stoichiometry $[Ru(C_2HR)(PPh_3)_2(\eta-C_5H_5)]PF_6$ (or BPh_4) (R = Me, Ph, C_6F_5 or CO_2Me, for example). The IR and NMR data [ν(CC) 1640 cm^{-1}; C*H* at τ 5.1t J_{HP} < 1Hz); Ru*C*CPh at 350 p.p.m.] are consistent with their formulation as the η^1-vinylidene complexes (I). In particular, the triplet found for the metal-bonded carbon in the ^{13}C NMR spectra occurs in the region (250-360 p.p.m.) usually associated with carbene complexes,[9] in contrast to the value of 112.8 p.p.m. found for $Pt(\eta^2-C_2Me_2)(PPh_3)_2$.[10] In the present case, the strong deshielding observed can be rationalised by the efficient back-bonding from the electron-rich metal centre into the strongly π-accepting vinylidene ligand. The vinylidene formulation is also supported by the large *gem* H-Me coupling (*ca*. 7Hz) found for (I; R = Me), obtained from prop-1-yne.

Deprotonation of the vinylidene complexes occurs on treatment with bases such as hydroxide, carbonate, or methylide, with formation of the corresponding σ-acetylide. The same reaction occurs on treatment of the cationic complexes with alumina, when the initially dark red-purple solutions rapidly change to the yellow of the neutral $Ru(C{\equiv}CR)(PPh_3)_2(\eta-C_5H_5)$ (II) complexes. These are readily isolated as yellow crystalline solids, and are characterised by their spectroscopic properties [ν(CC) *ca*. 2070 cm^{-1}, ^1H NMR, no resonance assignable to CH; ^{13}C NMR, ≡C at *ca*. 230 p.p.m.]. Compounds of this type have been reported previously, e.g. (II, R = CO_2Me) from the reaction between $RuMe(PPh_3)_2(\eta-C_5H_5)$ and HC_2CO_2Me,[11] and as copper(I) chloride adducts, from $RuCl(PPh_3)_2(\eta-C_5H_5)$ and CuC_2R.[12]

The stability of the cationic vinylidene complexes suggested that an alternative route to them might be via the protonation of the neutral ethynyl derivatives. Addition of HBF_4 or HPF_6 to $Ru(C_2Ph)(PPh_3)_2(\eta-C_5H_5)$ afforded directly at room temperature the phenylvinylidene complex (I), and other substituted ethynyl complexes react similarly. This reaction appears to have some general applicability to the formation of vinylidene complexes



(I)



(II)

from the corresponding σ-acetylides. However, *trans*-$Pt(C_2CF_3)_2(PEt_3)_2$ does not react with HPF_6 over 1 h at room temperature, while alkoxycarbene complexes are obtained from other platinum(II) acetylides and strong acids in alcohol solvents.[13]

There are several points of interest raised by this work, and we are currently investigating the factors which determine whether η^2-alkyne complexes, or the isomeric η^1-vinylidene complexes, are obtained from reactions between transition metal complexes and 1-alkynes.

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