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Preliminary communication

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# CYCLOPENTADIENYL-RUTHENIUM AND -OSMIUM CHEMISTRY. SOME REACTIONS OF SUBSTITUTED VINYLIDENE COMPLEXES.

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*Summary.* Reactions of $[Ru(C{:}CHPh)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ with MeOH, aqueous $HBF_4$ or $O_2$ afford $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta\text{-}C_5H_5)\}^+$, $Ru(CH_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$, and $[Ru(CO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ and $PhCO_2H$, respectively; alkylation of $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$ with $R'_3O^+PF_6^-$ gives complexes containing disubstituted vinylidene ligands, $[Ru(C{:}CRR')(PPh_3)_2(\eta\text{-}C_5H_5)]^+$.

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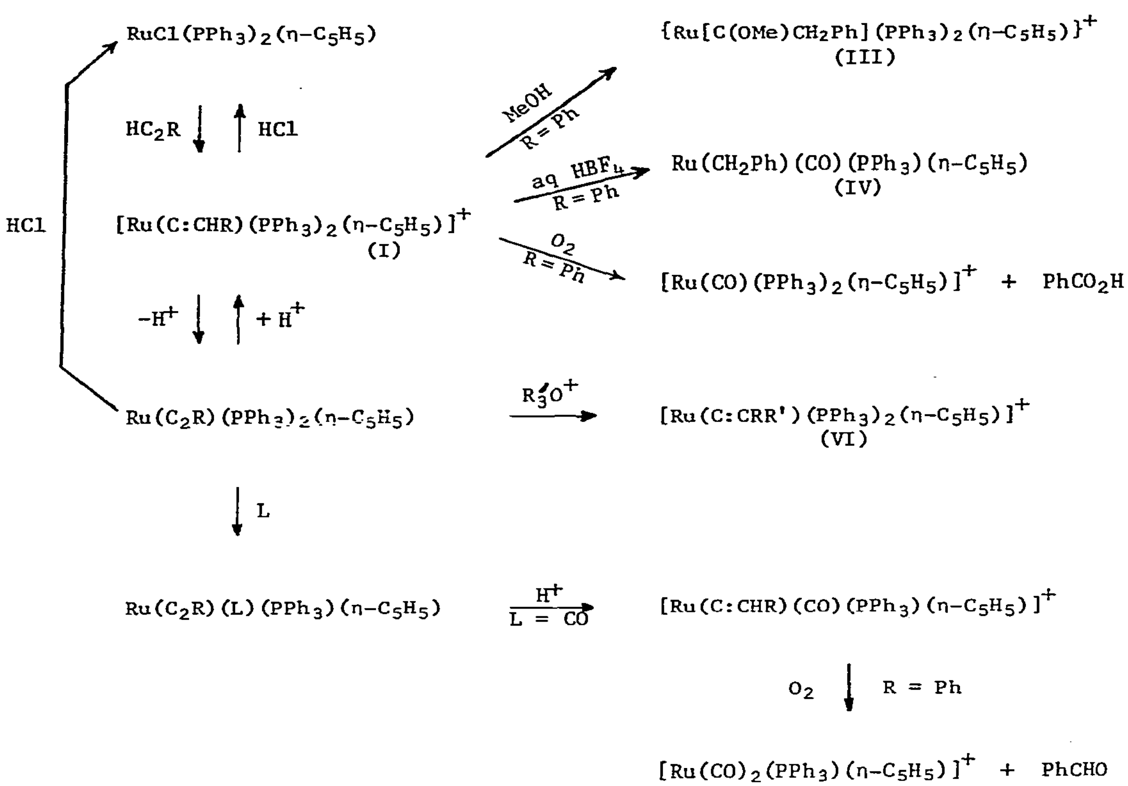
We have recently described the formation of substituted vinylidene complexes, $[Ru(C{:}CHR)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ (I), from terminal acetylenes (1-alkynes) and the chloride $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$, and their ready deprotonation to the corresponding σ-acetylides, $Ru(C_2R)(PPh_3)_2(\eta\text{-}C_5H_5)$.[1] Independently, and at about the same time, the complex $[Fe(C{:}CHPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ (II) was described,[2] being obtained from $Fe(C_2Ph)(CO)(PPh_3)(\eta\text{-}C_5H_5)$ and $HBF_4$ in $CH_2Cl_2$ or toluene; further examples of methyl, dimethyl and unsubstituted vinylidene complexes containing the $Fe(dppe)(\eta\text{-}C_5H_5)$ group have been reported.[3]

Vinylidene complexes have been implicated in several reactions of 1-alkynes with metal complexes, and particularly in the formation of alkoxycarbene complexes from 1-alkynes and *trans*-$PtRClL_2$.[4] It is obvious that the reactivity of the vinylidene ligand depends on both the metal and associated ligands, although the precise contributions of steric and electronic effects remain to be determined. Thus the reaction of (II) with methanol readily affords the corresponding alkoxycarbene complex,[2] whereas we find that (I; R = Ph) requires prolonged (several hours) heating in refluxing methanol to effect conversion to $\{Ru[C(OMe)CH_2Ph](PPh_3)_2(\eta-C_5H_5)\}PF_6$ (III) [$^1H$ NMR ($CDCl_3$): $\delta$ 3.4s ($OCH_3$), 4.8s ($C_5H_5$), 5.0s ($CH_2Ph$), 6.9-7.4m (Ph); $^{13}C$ NMR ($CDCl_3$): $\delta$ 62.7s ($OCH_3$), 63.2s ($CH_2$), 91.8s ($C_5H_5$), 127.1-137.5 ($C_6H_5$), 307.9t (RuC)] while the complexes $[Fe(C{:}CRR')(dppe)(\eta-C_5H_5)]^+$ (R,R' = H or Me) are unreactive towards alcohols.[3]

A second synthesis of the cationic vinylidene complexes (I) is direct protonation of the corresponding $\sigma$-acetylide with $HBF_4$ or $HPF_6$. Further reaction of (I; R = Ph) with aqueous $HBF_4$ affords the neutral benzyl complex $Ru(CH_2Ph)(CO)(PPh_3)(\eta-C_5H_5)$ (IV) [$\nu$(CO)($CHCl_3$) 1983 $cm^{-1}$; $^1H$ NMR ($CDCl_3$): $\delta$ 2.2t, 2.8q ($CH_2$), 4.6s ($C_5H_5$), 7.0-7.5m (Ph)]. In contrast, the reaction between $Fe(C_2Ph)(CO)_2(\eta-C_5H_5)$ and aqueous acid gives the acyl complex $Fe(COCH_2Ph)(CO)_2(\eta-C_5H_5)$,[5] and we note that $PtCl(C_2R)PMe_2Ph)_2$ reacts similarly.[6] Decarbonylation of acyl complexes to the corresponding alkyl is well-known, and in the present case, spontaneous intramolecular decarbonylation of an initial phenylacetyl complex occurs, with loss of $PPh_3$. We have shown previously that one of the $PPh_3$ ligands in $Ru(PPh_3)_2(\eta-C_5H_5)$ complexes is readily displaced by CO, a reaction ascribed to relief of steric strain.[7] The present reaction resembles the intermolecular decarbonylation of metal acyls by $RhCl(PPh_3)_3$,[8] and the formation of alkyl-carbonyl complexes by oxidative addition of acyl halides to iridium(I) centres.[9] The chloride $RuCl(PPh_3)_2(\eta-C_5H_5)$ is formed in reactions of $Ru(C_2R)(PPh_3)_2(\eta-C_5H_5)$ or (I) with HCl.

The electrophilic nature of the substituted vinylidene ligand is further demonstrated by the reaction of (I; R = Ph) with dioxygen in $CH_2Cl_2$ solution, which affords the carbonyl cation $[Ru(CO)(PPh_3)_2(\eta-C_5H_5)]^+$ [$\nu$(CO)($CHCl_3$) 1987 $cm^{-1}$], and benzoic acid as the isolable organic product. Similar oxidation of $[Ru(C{:}CHPh)(CO)(PPh_3)(\eta-C_5H_5)]BF_4$ (V) gives the dicarbonyl cation

SCHEME



$[Ru(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ [$\nu$(CO)($CHCl_3$) 1999, 1972 $cm^{-1}$], together with benzaldehyde. These reactions are interesting examples of the oxidative cleavage of C≡C triple bonds to CO (which remains coordinated to the metal) and an organic carbonyl product (aldehyde or carboxylic acid):

$$RC{\equiv}CH \rightarrow RHC{:}C \xrightarrow{[O]} CO + RC(O)H \xrightarrow{[O]} RC(O)OH$$

Reactions of (I) with bases are dominated by the facile deprotonation reaction.[1] We have found that alkylation of the $\sigma$-acetylides with trialkyloxonium salts affords a series of stable disubstituted vinylidene complexes, $[Ru(C{:}CRR')(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ (VI; R = Me or Et; R' = Me, Ph or $CO_2Me$), which are stable towards deprotonation. These derivatives are also reddish-purple, and have the characteristic low-field $^{13}C$ NMR signal at *ca.* 350 ppm, assigned to the metal-bonded carbon. The structure of (VI; R = R' = Me) has recently been confirmed by a single-crystal X-ray diffraction study.[10] This reaction significantly extends the range of substituted vinylidene complexes which are now accessible; the σ-acetylides are readily available, and complexes with a variety of ligands other than $PPh_3$ can be prepared by simple ligand exchange reactions, e.g. with CO, $CNBu^t$ or $P(OMe)_3$.

These reactions are summarised in the Scheme.

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## REFERENCES

1. M.I. Bruce and R.C. Wallis, *J.Organometallic Chem.*, 1978, 161, C1.
2. A. Davison and J.P. Solar, *J.Organometallic Chem.*, 1978, 155, C8.
3. A. Davison and J.P. Selegue, *J.Amer.Chem.Soc.*, 1978, 100, 7763; we have also obtained $[Ru(C{:}CH_2)(PPh_3)_2(\eta\text{-}C_5H_5)]PF_6$ directly from $C_2H_2$ and $RuCl(PPh_3)_2(\eta\text{-}C_5H_5)$ in the presence of $NH_4PF_6$: M.I. Bruce and J.D. Walsh, unpublished results.
4. M.H. Chisholm and H.C. Clark, *Accounts Chem. Res.*, 1973, 6, 202.
5. O.M. Abu Salah and M.I. Bruce, *J.C.S. Dalton*, 1974, 2302.
6. R.A. Bell, M.H. Chisholm, D.A. Couch and L.A. Rankel, *Inorg.Chem.*, 1977, 16, 677.
7. T. Blackmore, M.I. Bruce and F.G.A. Stone, *J.Chem.Soc.(A)*, 1971, 2376.
8. J.J. Alexander and A. Wojcicki, *J.Organometallic Chem.*, 1968, 15, P23.
9. M.A. Bennett, R. Charles and T.R.B. Mitchell, *J.Amer.Chem.Soc.*, 1978, 100, 2737.
10. R.E. Davis, personal communication (1978).