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THE NATURE OF MONONUCLEAR RUTHENIUM CARBONYL COMPLEXES IN STRONGLY ACIDIC SOLUTIONS

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Summary

The cationic complexes $HRu(CO)_5^+$ and $HRu(CO)_4L^+$ ($L = P(C_6H_5)_3$) were prepared in situ by extracting hexane solutions of the neutral complexes $Ru(CO)_5$ and $Ru(CO)_4L$ with concentrated H_2SO_4. The ^{13}C NMR spectra showed both cations to be nonfluxional on the NMR time scale at 25°C and the $HRu(CO)_4L^+$ species to have the *cis* configuration.

There has been considerable recent interest in the catalysis chemistry of ruthenium carbonyl complexes in acidic solutions. This interest includes work on the homogeneous catalysis of the water gas shift reaction in acidic diglyme solutions [1] as well as recent reports of the hydrogenation of carbon monoxide and syngas homologation of aliphatic carboxylic acids, both catalyzed by ruthenium carbonyls in acetic acid solutions [2,3]. Given that under the CO pressures used for these catalysts mononuclear ruthenium species would be expected to play significant roles, we have prepared and characterized spectrally the simplest carbonyl hydride cation $HRu(CO)_5^+$ and its monosubstituted derivative $HRu(CO)_4L^+$ (L = triphenylphosphine).

Results and discussion

Solutions of $Ru(CO)_5$ and $Ru(CO)_4L$ in hexane were prepared by photolyzing hexane solutions of the trinuclear clusters $Ru_3(CO)_{12}$ and $Ru_3(CO)_9L_3$ respectively under a CO atmosphere [4]. Pale yellow solutions of the respective cations are formed upon extraction of the hexane solutions with CO saturated conc. H_2SO_4. These solutions are indefinitely stable at room temperature under CO.

The ^1H NMR spectrum of the $HRu(CO)_5^+$ solution at room temperature displays a singlet in the metal hydride region at δ — 7.23 ppm while the $^{13}C\{^1H\}$ NMR spectrum of a sample prepared from 40% ^{13}C enriched $Ru_3(CO)_{12}$ showed

TABLE 1

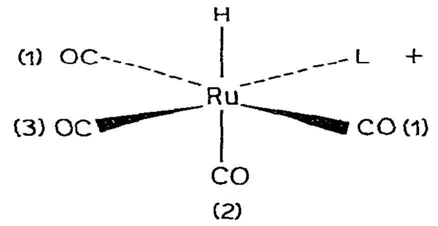
^{13}C NMR SPECTRA OF MONONUCLEAR RUTHENIUM CARBONYLS

Complex	δ^{13}C(ppm)	$^2J(^1H—^{13}C)$(Hz)	$^2J(^{13}C—^{31}P)$(Hz)
$HRu(CO)_5^+$ *cis*	180.46 [a]	<4	
trans	178.23	24	
$Ru(CO)_4(PPh_3)$	204.38 [b]		4
$HRu(CO)_4(PPh_3)^+$(1)	185.58 [a]	4	13
(2)	183.30	24	8
(3)	182.87	<2	69

[a] In concentrated H_2SO_4, 25°C. [b] In hexane, 25°C.

two singlets at 180.46 and 178.48 ppm in an approximately four to one intensity ratio. The proton coupled ^{13}C spectrum displays a broadened signal at 180.57 ppm ($^2J(^{13}C—^1H) < 4$ Hz) and a doublet centered at 178.23 ppm ($^2J(^{13}C—^1H) = 24$ Hz). These data are consistent with the $HRu(CO)_5^+$ formulation as a hexacoordinate ion and assignment of the 180.46 and 178.48 ppm resonances to the *cis* and *trans* carbonyls, respectively. Notably the observation of both resonances indicates the complex to be nonfluxional on the NMR time scale at room temperature.

The ^{1}H NMR spectrum of $HRu(CO)_4L^+$ in room temperature conc. H_2SO_4 displayed a doublet in the metal hydride region at δ — 6.53 ppm with a splitting of 14 Hz. The ^{31}P NMR of the same solution displayed a doublet at 29.23 ppm * with the same splitting, thus indicating coupling to a single proton with $^2J(^1H—^{31}P) = 14$ Hz. The relatively small $^1H—^{31}P$ coupling suggests the *cis* configuration [$^2J(^1H—^{31}P_{trans}) = 80—150$ Hz while $J(^1H—^{31}P_{cis}) = 10—40$ Hz in comparable compounds [5]]. The ^{13}C NMR spectrum of an enriched $HRu(CO)_4L^+$ solution on a 20 MHz instrument gave a poorly resolved multiplet in the 180—185 ppm region. However, the $^{13}C\{^1H\}$ spectrum measured on the 125 MHz instrument of the NSF Regional NMR Facility at the California Institute of Technology displayed three resolvable doublets centered at 185.58, 183.30 and 182.87 ppm with coupling constants $^2J(^{13}C—^{31}P)$ of 13, 8 and 69 Hz, respectively (Table 1). The integrated intensity of the first resonance was twice that of each of the latter two, which were equal. The ^{1}H coupled spectrum afforded additional splitting of the resonances at 185.58 ppm ($^2J(^{13}C—^1H) = 4$ Hz) and 183.30 ppm ($^2J(^{13}C—^1H) = 24$ Hz). These data (Table 1) can be interpreted in terms of a *cis* geometry A for $HRu(CO)_4L^+$ with assign-



A

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* Relative to phosphoric acid contained in a concentric capillary; downfield shifts are assigned positive values.

ment of the resonances at 183.30 ppm assigned to position (2); at 182.87 ppm to position (3) [large $J(^{13}C—^{31}P)$ hence *trans* to L] and at 185.58 ppm to the two mutually *trans* CO's at position (1). Resolution of these resonances indicates the ion to be nonfluxional and the observation of a single metal hydride in the ^1H NMR spectrum suggests that the *cis* configuration is favoured over the *trans* isomer by a factor of at least ten to one. The *cis* configuration is consistent with that seen for other disubstituted $Ru^{(II)}$ tetracarbonyls $Ru(CO)_4X_2$ ($X = H^-, Cl^-$, etc.) [6]. The ^{13}C NMR spectrum of the neutral complex $Ru(CO)_4L$ in hexane exhibits one doublet at 204.38 ppm ($^2J(^{13}C—^{31}P) = 4$ Hz) indicating this species to be stereochemically nonrigid at room temperature. Similarly, the analogous compound with $L = P(OCH_3)_3$ shows fluxional behavior to —120°C in freon solution [7].

Although the ions $HFe(CO)_5^+$ and $HOs(CO)_5^+$ have been characterized earlier [8] and $HRu(CO)_5^+$ mentioned in a footnote [8], the present report represents the first ^{13}C NMR study of any series member. Given the stereochemical rigidity of other hexacoordinate metal hydride carbonyls such as $Ru(CO)_4H_2$, $Os(CO)_4H_2$, $Mn(CO)_5H$ and $Re(CO)_5H$ [6a], it is not surprising that the ions $HRu(CO)_5^+$ and $HRu(CO)_4L^+$ are also nonfluxional. However, it is notable that simple protonation has such a dramatic effect on the stereomobility of such systems.

Experimental

Materials and syntheses

Triruthenium dodecacarbonyl, $Ru_3(CO)_{12}$, was prepared from hydrated ruthenium trichloride by the method of Dawes et al. [9]. The symmetrically substituted trinuclear complex $Ru_3(CO)_9(PPh_3)_3$ was prepared by the published procedure [10].

The mononuclear complexes $Ru(CO)_5$ or $Ru(CO)_4(PPh_3)$ were prepared by phtolysis of either $Ru_3(CO)_{12}$ (50 mg, 0.08 mmol) or $Ru_3(CO)_9(PPh_3)_3$ (100 mg 0.08 mmol) in 50 ml of solvent, hexane or toluene, respectively, under a CO atmosphere. The photolysis lamp was a Welch scientific UV lamp and the light was filtered through the Pyrex glass of the reaction vessel. The extent of conversion from trimer to monomer was determined by monitoring the IR spectrum of the solution. Solutions of the cations $[HRu(CO)_5]^+$ and $[HRu(CO)_4(PPh_3)]^+$ were prepared by extracting hexane solutions of the relevant neutral complex with conc. sulphuric acid (1 cc) under a CO atmosphere.

NMR spectra

Proton spectra were obtained on a Varian Associates XL-100 NMR spectrometer operating in the C.W. mode using D_2O as a lock substance and external standard. Phosphorus-31 spectra were also obtained on an XL-100 spectrometer operating in the F.T. mode using CD_2Cl_2 as a lock substance and 85% phosphoric acid as an external standard.

Carbon-13 NMR spectra were obtained on a Varian Associates C.F.T. 20 or a Brüker W.M. 500 NMR spectrometer operating in the F.T. mode using $CDCl_3$ as a lock substance and an external reference. All spectra were obtained at ambient temperature.

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