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PROTONATION OF METAL CARBONYL COMPLEXES

IV. AN INFRARED STUDY OF THE CYCLOPENTADIENYL COMPLEXES OF VANADIUM, NIOBIUM AND RHENIUM

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SUMMARY

Protonation in acidic media of compounds of the type $(\pi\text{-}C_5H_5)M(CO)_4$ (M = V,Nb) and $(\pi\text{-}C_5H_5)Re(CO)_3$ and their phosphine derivatives has been studied by IR spectroscopy. The results obtained and those from previous studies indicate that for cyclopentadienyl carbonyl complexes of Group V and VII elements with the same ligand L the basicity of the metal atom increases in the series $CpMn(CO)_2L < CpV(CO)_3L < C_6H_6Cr(CO)_2L < CpRe(CO)_2L < CpNb(CO)_3L$.

INTRODUCTION

In previous papers in this series[1-3], it has been shown via IR and NMR spectroscopic methods that in acidic media phosphine derivatives of benzenechromium tricarbonyl and cyclopentadienylmanganese tricarbonyl undergo protonation at the metal atom. Such protonation is accompanied by a noticeable shift of the CO stretching modes in the IR spectrum to the high frequency region (100–150 cm^{-1}) and for complexes of the type $ArCr(CO)_2PPh_3$ this was accompanied by the appearance of a signal corresponding to the proton attached to the metal atom in the high field region of the PMR spectra. Ease of protonation increases with increasing electron-donor properties of both the π-ring substituents and the phosphine ligands attached to the metal atom.

In the present work protonation of compounds of the type $CpM(CO)_4$ (M = V, Nb) and $CpRe(CO)_3$ and their phosphine derivatives is studied.

RESULTS AND DISCUSSION

The observed CO stretching frequencies for solutions of the compounds studied in CH_2Cl_2/acid mixtures are listed in Table 1. The type of spectral change observed upon protonation is the same as that reported in previous papers[1-3], a 100–150 cm^{-1} shift in the CO stretching mode to the high frequency region of the spectrum occurring in each case.

TABLE 1

STRETCHING MODE FREQUENCIES $\nu(CO)$ (cm^{-1}) FOR THE CYCLOPENTADIENYL CARBONYL DERIVATIVES OF RHENIUM, VANADIUM AND NIOBIUM IN VARIOUS SOLVENTS

Compound	*CH_2Cl_2 (non-protonated form)*	*Protonated form*		*Mixture where only protonated form was observed*
		In CH_2Cl_2/HCl	*In CF_3COOH/CH_2Cl_2*	
$CpRe(CO)_3$	1931, 2026			
$CpRe(CO)_2PPh_3$	1859, 1930		1922, 2053	1/10
$CpV(CO)_4$	1930, 2032			
$CpNb(CO)_4$	1920, 2036		2087, 2145	1/1
$CpV(CO)_3PPh_3$	1855, 1955		2045, 2080	1/1
$CpNb(CO)_3PPh_3$	1850, 1960		2050, 2100 2035 (sh)	1/90
$CpNb(CO)_3P(C_6H_{11})_3$	1840, 1950		2043, 2094 2028 (sh)	1/100
$CpNb(CO)_2(PPh_3)_2$	1773, 1870	1983, 2023	1980, 2040	$<1/100$
$CpNb(CO)_2(Ph_2PCH_2CH_2PPh_2)$	1787, 1875	1985, 2040	1987, 2042	$<1/100$

Cyclopentadienylrhenium tricarbonyl, in a similar manner to the corresponding manganese complex[3], is not protonated in trifluoroacetic acid media, but its monophosphine derivative $CpRe(CO)_2 \cdot PPh_3$ is protonated in both CF_3COOH and CF_3COOH/CH_2Cl_2 mixtures. Even when the composition of the mixture was 1/10 only the protonated form of this complex was observed. When the composition was varied to 1/25, both protonated and non-protonated forms were found to be present in approximately equal quantities. In the case of $CpMn(CO)_2PPh_3$ only partial protonation occurs even in pure CF_3COOH. Thus the metal atom in the rhenium complex exhibits a much higher basicity than the manganese atom in the corresponding manganese compound.

Cyclopentadienylvanadium tetracarbonyl is not protonated in CF_3COOH media, but $CpNb(CO)_4$ is protonated both in pure CF_3COOH and in a 1/1 CF_3COOH/CH_2Cl_2 mixture. Even when the composition is changed to 1/10 the protonated form is still noticeable. In the IR spectra of the resulting solutions, bands corresponding to the protonated form appear at 2087 and 2145 cm^{-1} in contrast to those of the parent compound which appear at 1920 and 2036 cm^{-1}. From this it follows that the niobium atom in $CpNb(CO)_4$ has a much higher basicity than the vanadium atom in $CpV(CO)_4$. However it should be noted that in contrast to compounds investigated previously protonation in this case is accompanied by an additional phenomenon, *i.e.* the spectrum obtained is time-dependent, the bands corresponding to the protonated form disappearing with time while new bands appear and grow near 2010 and 2075 cm^{-1} due to formation of trifluoroacetic derivatives through the replacement of CO ligands in the complex. This process is not reversible; the bands do not disappear when the solution is diluted with methylene chloride, and their intensity increases with time. The bands corresponding to the protonated form also disappear upon addition of PPh_3 to the solution. A decrease in the charge at the protonated metal atom facilitates nucleophilic attack by the phosphine molecule and leads to the substitution of the carbonyl groups. The bands of the trifluoroacetate derivatives are not affected by addition of PPh_3. Furthermore, no change occurs when PPh_3 is added to the CH_2Cl_2 solution in the absence of acid.

Monophosphine derivatives of the type $CpM(CO)_3PPh_3$ also demonstrate the higher basicity of the niobium atom. It has been shown[1-3] that the introduction of a phosphine molecule into the complex facilitates protonation in both vanadium and niobium derivatives. But for $CpNb(CO)_3PPh_3$ in a 1/90 mixture of CF_3COOH/CH_2Cl_2, only the protonated form was observed and for $CpV(CO)_3PPh_3$ in a 1/10 mixture only of the same solvents the protonated form was noted. In fact, with the latter complex complete protonation occurs in a 1/1 solvent mixture. The process of protonation is, however, reversible. Dilution of the solution with CH_2Cl_2 leads to an increase in the concentration of the non-protonated form and to a decrease in that of the protonated variety. With the vanadium complex, additional interaction with CF_3COOH takes place and this is accompanied by the appearance of new bands at 2020 and 2070 cm^{-1}. These bands do not disappear on dilution and consequently are not due to the protonated form. When the acidity is low (1/10), bands corresponding to the protonated form are not observed, the only reaction being that with CF_3COOH. In the initial stages, however, bands at 2020 and 2070 cm^{-1} appear in the IR spectrum, and this is followed by the disappearance of all the carbonyl bands. This latter process is accompanied by the evolution of CO.

Tricyclohexylphosphine is a more powerful donor ligand than triphenylphosphine and $CpNb(CO)_3P(C_6H_{11})_3$ is more readily protonated than $CpNb(CO)_3$-PPh_3 in accordance with the regularities established earlier. With this complex, bands corresponding to the protonated form were observed in a 1/120 mixture of CF_3COOH/CH_2Cl_2.

The addition of PPh_3 to an acid solution of $CpV(CO)_3PPh_3$ leads to the rapid decomposition of this compound, but under the same conditions the monophosphine derivatives of $CpNb(CO)_4$ are stable. At room temperature, and in the absence of irradiation, it is most probable that the first stage in the reaction is a nucleophilic attack on the metal atom and that this is followed by displacement of a CO group (associative mechanism). The higher basicity of the niobium atom impedes this nucleophilic attack in good agreement with the observed protonation data. The basicity of the metal atom is lower in the protonated complex $CpNb(CO)_4H^+$ than in the phosphine derivative and this makes substitution of CO groups more probable. No spectral changes occur when PPh_3 is added to the neutral solution, while addition of PPh_3 to the acidic solution probably facilitates substitution of the CO groups by trifluoroacetate either through proton capture and because the coordination site near the metal atom becomes vacant or alternatively because the formation of the anion CF_3COO^- is facilitated.

The bisphosphine derivatives $CpNb(CO)_2(PPh_3)_2$ and $CpNb(CO)_2(Ph_2PCH_2 \cdot CH_2PPh_2)$, where the basicity of the metal is higher than in the monophosphine derivatives, are protonated not only in mixtures of CF_3COOH/CH_2Cl_2 but also in CH_2Cl_2 solutions saturated with HCl. Addition of PPh_3 to acid solutions of these complexes induces no spectral changes in accordance with the high basicity of the metal.

Our results clearly show that the niobium and vanadium cyclopentadienyl carbonyl complexes undergo protonation in acid media, but that the reaction is sometimes accompanied by other processes. The position of the protonation equilibrium depends upon the acidity of the medium and on the type and number of phosphine ligands. Increasing the donor properties of the ligand increases the basicity of metal atom and shifts the equilibrium towards the protonated form. The vanadium atom has a lower basicity relative to the niobium atom in similar complexes. The data obtained in this work and that obtained previously[3] show that in the cyclopentadienyl carbonyl complexes of Group V and VII transition metals the basicity of metal atom increases as the atomic number of the element in a particular group increases. The compounds investigated here may be arranged in the following series of increasing basicity where the ligand L is the same in each complex: $CpMn(CO)_2L < CpV(CO)_3L < C_6H_6Cr(CO)_2L < CpRe(CO)_2L < CpNb(CO)_3L$.

EXPERIMENTAL

The IR spectra were measured with a Zeiss UR-20 spectrometer using an LiF prism. The instrument was calibrated using the DCl vibration–rotation spectrum. Solution preparation and cell filling were performed under an argon atmosphere, the spectra being recorded immediately after preparation of the solutions.

All compounds were synthesized by previously described methods[4,5], with the exception of cyclopentadienylniobium tricarbonyl tricyclohexylphosphine which was prepared as follows: 1.2 g π-$C_5H_5Nb(CO)_4$ and 2.8 g $P(C_6H_{11})_3$ were irradiated with UV light in boiling benzene (20 ml) under an argon atmosphere over a period of 5 h. After cooling, the mixture was filtered through a layer of Al_2O_3 5 cm in thickness. The filtrate was concentrated *in vacuo* and after dilution with n-hexane yellow crystals were precipitated. Yield of π-$C_5H_5Nb(CO)_3P(C_6H_{11})_3$ was 50%. (Found: C, 59.80; H, 7.48%. $C_{26}H_{38}O_3PNb$ calcd.: C, 59.76; H, 7.36%.)

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