

TRIVALENT PHOSPHORUS DERIVATIVES OF GROUP VIA

IV. INFRARED AND PMR STUDIES OF THE PROTONATION OF $M(\text{CO})_{6-n}(\text{PA}_3)_n$ COMPLEXES ($M = \text{Mo}, \text{W}; A = \text{CH}_3, \text{OCH}_3; n = 2, 3, 4$)

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Summary

The action of trifluoroacetic acid on the series $M(\text{CO})_{6-n}(\text{PA}_3)_n$ ($M = \text{Mo}, \text{W}; A = \text{CH}_3, \text{OCH}_3; n = 2, 3, 4$) has shown that protonation occurs if $n \geq 3$. For $n = 3$ the basicity of the ligand PA_3 plays a more important role in the stability of $[\text{HM}(\text{CO})_3(\text{PA}_3)_3]^+$ complexes than for $n = 4$. Infrared and proton NMR give evidence of the stereochemical non-rigidity of the $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ heptacoordinated cation.

Introduction

In spite of the great number of studies on the protonation of metal carbonyl complexes [1] no systematic study of the protonation of the $M(\text{CO})_{6-n}(\text{PA}_3)_n$ series has been made, although this study can give some insight into the factors governing the stability of the metal–hydrogen bond in $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ compounds; indeed, a previous study on arene chromium tricarbonyl complexes has shown that the ease of protonation increases with the introduction of increasing electron-releasing substituents into the π -bonded aromatic ring [2,3]. In the same way protonation of $M(\text{PA}_3)_6$ and $M\text{CO}(\text{PA}_3)_5$ complexes has revealed the great importance of the basicity of PA_3 ligands [4].

In our case three factors are expected to affect the stability of the metal–hydrogen bond: the basicity of PA_3 ligands, the degree of replacement of carbonyl groups n and, perhaps to a lesser extent, the nature of the metal. We have therefore studied the protonation of the series $M(\text{CO})_{6-n}(\text{PA}_3)_n$ with two ligands of different basicity, $\text{P}(\text{OCH}_3)_3$ and $\text{P}(\text{CH}_3)_3$, and with the two metals, molybdenum and tungsten.

Results and discussion

Protonation has been studied, depending on the substrate, either in pure trifluoroacetic acid or in a mixture of the acid with dichloromethane. No protonation occurs for $n = 2$ and addition of the pure acid only induces decomposition to $M(\text{CO})_5\text{PA}_3$ and $M(\text{CO})_6$ compounds. For $n = 3$ the situation is more complex; in pure trifluoroacetic acid protonation occurs in the two cases where $A = \text{CH}_3$ or OCH_3 , but different behaviour is revealed on dilution. For $A = \text{OCH}_3$ in a 50/50 mixture of CF_3COOH and CH_2Cl_2 both the protonated and the non-protonated forms are observed. On the other hand for $A = \text{CH}_3$ even in a 1/100 mixture of $\text{CF}_3\text{COOH}/\text{CH}_2\text{Cl}_2$ only the protonated form occurs.

For $n = 4$ the complexes of both ligands protonate in the same range of concentration of trifluoroacetic acid. Moreover, the protonated complexes with $A = \text{CH}_3$ have been isolated with the PF_6^- anion.

Infrared results

Infrared spectroscopy is a valuable tool in the study of the protonation of metal carbonyl complexes [2]. Protonation at the metal reduces its formal charge and leads to a decrease of charge transfer from the metal to the carbonyl group. This induces an increase in the CO stretching frequencies.

The results of the infrared spectra are gathered in Table 1. They show a shift to higher frequencies of about $80\text{--}90\text{ cm}^{-1}$ and strongly suggest that protonation has occurred on the metal atom.

TABLE 1
INFRARED SPECTRA IN THE CO STRETCHING FREQUENCIES OF $M(\text{CO})_{6-n}(\text{PA}_3)_n$ AND THEIR PROTONATED FORM

Compounds	Hexadecane solution	Protonated form
<i>fac</i> -Mo(CO) ₃ [P(OCH ₃) ₃] ₃	1977 s	2065 m
	1926 s	1975 s
	1916 s	1922 s
<i>fac</i> -Mo(CO) ₃ [P(CH ₃) ₃] ₃	1945 s	2037 m
	1841 s	1955 (sh)
		1930 s
<i>fac</i> -W(CO) ₃ [P(CH ₃) ₃] ₃	1940 s	2033 m
	1844 s	1945 (sh)
		1925 s
<i>mer</i> -Mo(CO) ₃ [P(CH ₃) ₃] ₃	1962 w	2037 m
	1854 s	1955 (sh)
		1930 s
<i>cis</i> -Mo(CO) ₂ [P(CH ₃) ₃] ₄	1860 s	1943 s
	1800 s	1870 s
		1935 s
<i>cis</i> -W(CO) ₂ [P(CH ₃) ₃] ₄	1858 s	1935 s
	1796 s	1925 (sh)
		1855 s
<i>cis</i> -Mo(CO) ₂ [P(OCH ₃) ₃] ₄	1909 s	1820 m
	1856 s	1997 m
		1915 s
<i>cis</i> -W(CO) ₂ [P(OCH ₃) ₃] ₄	1905 s	1995 m
	1845 s	1915 s
		1855 m

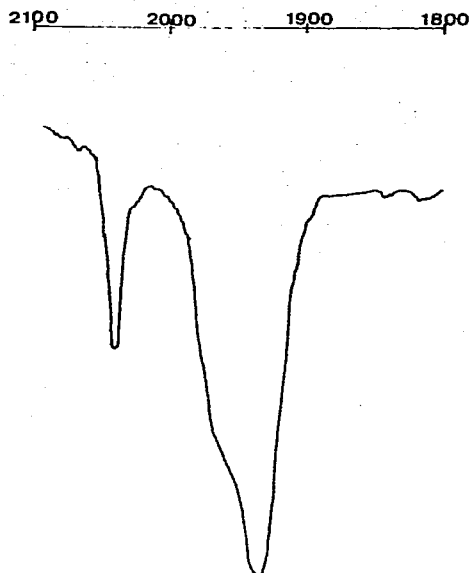


Fig. 1. Infrared spectra of $[\text{HMo}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$.

For $n = 3$ it immediately appears that following protonation, the number of infrared bands in the region of the CO stretching frequencies increases from two to three (Fig. 1). The use of deuterated trifluoroacetic acid precludes any attribution to M—H stretching frequencies.

This increase does not seem to be due to the splitting of the E band expected for a C_{3v} point group of carbonyl ligands because if this happened the two resulting bands would be of the same intensity [5]. Therefore the group of the three CO must be of lower symmetry, C_s or C_{2v} .

Another important fact is that protonation of *fac* or *mer* leads to the same spectra and this strongly suggests an identical protonated form for the two isomers. Furthermore, by allowing a base such as $\text{P}(\text{C}_4\text{H}_9)_3$ to react with the protonated complexes, we obtained a mixture of *fac*- and *mer*- $\text{M}(\text{CO})_3(\text{PA}_3)_3$.

For $n = 4$ the tungsten complexes exhibit three bands and the molybdenum complexes only two bands. The band of lower frequency in the case of tungsten complexes has been attributed to metal—hydrogen stretching because of its medium intensity and its disappearance when we used deuterated trifluoroacetic acid. Furthermore, as shown in Fig. 2, the appearance of the infrared spectra is quite different for $\text{A} = \text{CH}_3$ and $\text{A} = \text{OCH}_3$. This suggests either a different structure for compounds with $\text{A} = \text{OCH}_3$ (for instance an opening of the CO—M—CO angle) or a mixture of isomers; indeed it has recently been found [6] that the $[\text{HM}(\text{CO})_2(\text{dmpe})_2]^+$ complexes [dmpe = bis(dimethylphosphino)ethane] have two isomers *cis* and *trans* (referring to the mutual CO positions) with, respectively two and one infrared CO stretching frequencies. This observation could also explain why the $[\text{HW}(\text{CO})_2(\text{P}(\text{CH}_3)_3)_4]^+$ complex exhibits a third weak CO stretching band as a shoulder of the higher energy band.

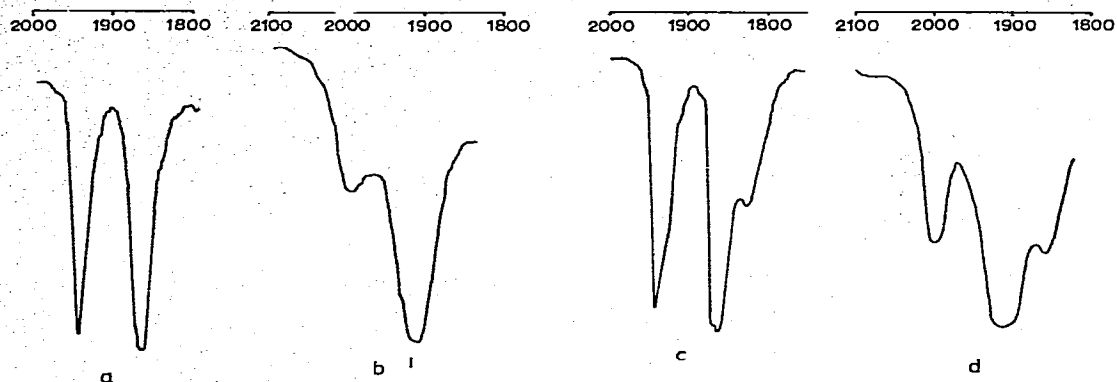


Fig. 2. Infrared spectra of: (a) $[\text{HMo}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$; (b) $[\text{HMo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_4]^+$; (c) $[\text{HW}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$; (d) $[\text{HW}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_4]^+$.

In summary, examination of the infrared results provokes two main observations:

(1) Protonation, as was expected, induces a 80-90 cm^{-1} shift to higher frequencies of the CO stretching bands.

(2) Protonation seems to be accompanied by a structural change as can be seen either from the increase in the number of CO bands ($n = 3$) or from the variation of their intensity ratio ($n = 4$).

Proton NMR results

Proton NMR is certainly the most useful tool in the study of protonation of metal complexes because the hydrogen bonded to metal give a resonance at high field relative to TMS (tetramethylsilane) [7].

In Table 2 are gathered the details of the proton NMR spectra of the $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ complexes.

As was expected, all the products studied show a resonance in the high

TABLE 2
PROTON NMR DATA FOR $\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n^+$ COMPLEXES

Compounds	τ , OCH_3	τ , CH_3	τ , H	$J(\text{PHlig.})$	$J(\text{PH})^a$
$[\text{HMo}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$		8.24	14.31	8.5	43(q)
$[\text{HMo}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_3]^+$	6.17		15.20	11.5	32(q)
$[\text{HW}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$		8.54	13.88	8.8	47(q)
$[\text{HW}(\text{CO})_3[\text{P}(\text{OCH}_3)_3]_3]^+$	6.17		14.75	11	41(q)
$[\text{HMo}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$		8.50	12.55	6	^b
		8.09		8	
$[\text{HMo}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_4]^+$	6.20		15.83	unresolved	36(qt)
$[\text{HW}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$		8.20	13.66	6.0	^b
		8.34			
$[\text{HW}(\text{CO})_2[\text{P}(\text{OCH}_3)_3]_4]^+$	6.35		15.41	unresolved	41(qt)

^a q = quartet; qt = quintet. ^b See text.

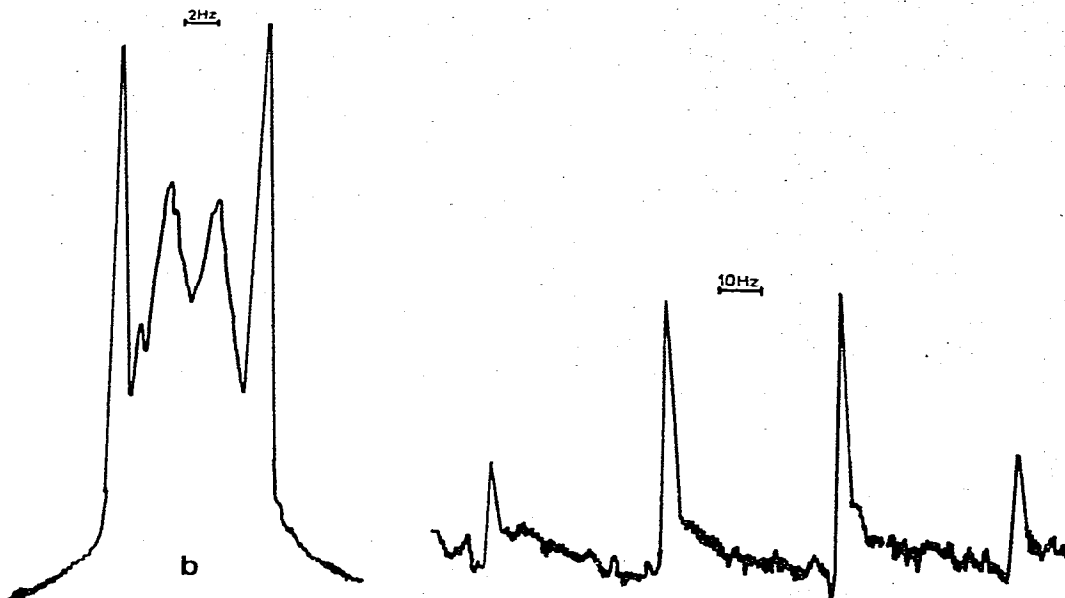


Fig. 3. ^1H NMR resonance of $\text{P}(\text{CH}_3)_3$ in $[\text{HMo}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$.

Fig. 4. Hydride resonance in $[\text{HMo}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$

field region ($13 < \tau < 16$) characteristic of the metal—hydrogen bond. Attention must be drawn to the particular behaviour of $\text{P}(\text{OCH}_3)_3$ complexes. Trifluoroacetic acid hydrolyses this ligand and the spectra must be run quickly. But in these conditions we are sure that what we have observed is only the expected protonated form because hydride resonance appears in the first stage of the running of NMR spectra and no further signal appears in this part of the spectrum.

For $n = 3$ spectra have been observed in solution in pure trifluoroacetic acid.

In the case where $\text{A} = \text{CH}_3$, the signal from the $\text{P}(\text{CH}_3)_3$ ligand is of the type $\text{AA}'\text{A}''\text{XnX}'\text{nX}''\text{n}$ [8] (Fig. 3). In the high field part (relative to TMS) there is a 1.3.3.1 quartet which shows that the hydride is equally coupled to the three phosphorus ligands (Fig. 4). This quartet is in the ratio 1/27 relative to the $\text{P}(\text{CH}_3)_3$ resonance which confirms the $[\text{HM}(\text{CO})_3[\text{P}(\text{CH}_3)_3]_3]^+$ formulation.

Moreover, in confirmation of the infrared results we have also found by proton NMR that the *mer* isomers give the same spectra as the *fac* isomers.

In the case where $\text{A} = \text{OCH}_3$, immediately after dissolution in trifluoroacetic acid the OCH_3 resonance appears as a doublet and the hydride resonance is a 1.3.3.1 quartet. Also, in this case, protonation of *mer* or *fac* isomers leads to the same spectra.

For $n = 4$, spectra have been observed in a mixture of trifluoroacetic acid and dichloromethane. In the case where $\text{A} = \text{CH}_3$, the ligand signal appears as two triplets in 1/1 ratio for $\text{M} = \text{Mo}$ and a doublet and a broad signal in the same ratio for $\text{M} = \text{W}$. For $\text{M} = \text{Mo}$ the hydride resonance gives seven peaks with relative intensities 1.2.3.4.3.2.1 (Fig. 5a). For $\text{M} = \text{W}$ there are nine resonances some

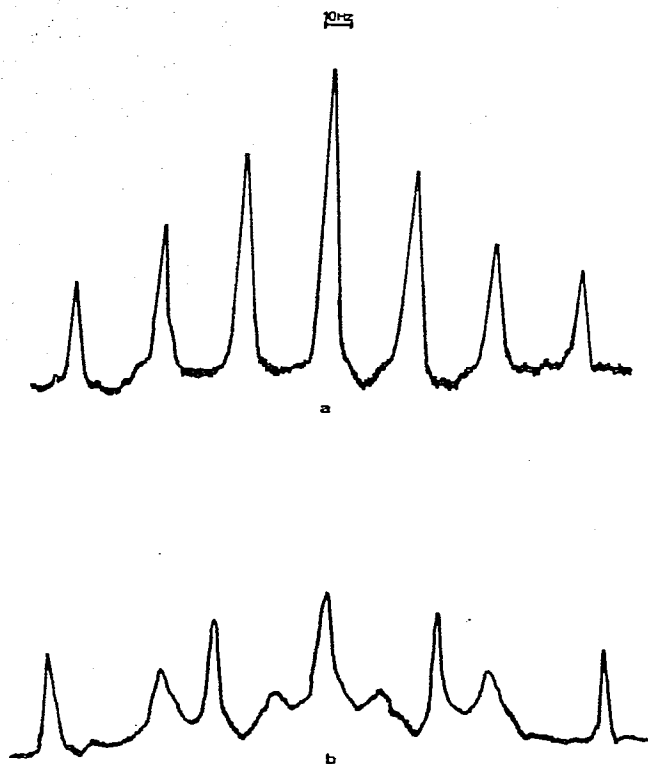


Fig. 5. Hydride resonance in: (a) $[\text{HMo}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$; (b) $[\text{HW}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$.

of which are broad (Fig. 5b). In the case where $\text{A} = \text{OCH}_3$ the OCH_3 resonance is broad and non-resolved and the hydride signal appears as a quintet showing that the hydride is equally coupled to the four phosphorus ligands.

Spectroscopic results and structure of $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ complexes

The compounds studied here are seven-coordinate and three main structures have been found for this coordination number:

- (i) pentagonal bipyramid,
- (ii) capped octahedron,
- (iii) an arrangement where the seventh ligand is inserted above the centre of one of the rectangular faces of a trigonal prism.

In the field of carbonyl transition metal complexes, such as $\text{MoBr}_2(\text{CO})_3\text{-}(\text{dpe})$ [9] [dpe = bis(diphenylphosphine)ethane] for instance, the most common arrangement found is the capped octahedron. Furthermore the same arrangement exists in another very similar complex: $\text{TaH}(\text{CO})_2(\text{dmpe})_2$ [10]. The hydrogen occupies the capped face.

On the basis of these results let us now examine the possible structure of $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ complexes for each degree of substitution.

$n = 3$. From the infrared results we have seen that the local symmetry of the CO group has been lowered and from the NMR results it appears that the three ligands are equivalent and equally coupled to the hydride ligand. These

two observations are not consistent with one of the three structures known for heptacoordination; indeed, the NMR results would be only consistent with the capped octahedron where the hydride would occupy the capped face formed by either the three phosphorus ligands or the three carbonyl groups, but in this case the C_{3v} symmetry of the CO groups would be preserved and this disagrees with the infrared results.

Thus we have to consider an exchange phenomenon which is quite common in heptacoordination and which is also consistent with the fact that the *mer*- and *fac*- $M(\text{CO})_3(\text{PA}_3)_3$ complexes give the same protonated form.

$n = 4$. An important fact in this series is the great difference observed for the spectrographic results when $A = \text{CH}_3$ or OCH_3 . When $A = \text{CH}_3$ infrared results show that the geometry of the CO groups is only slightly affected by protonation. Similarly, from proton NMR results the two groups of phosphine ligands are preserved. Thus it seems that protonation has only slightly affected the geometry of the initial complexes.

However, examination of the geometries based on a capped octahedron, which is the most consistent with these observations, shows that it is not possible to render an account of the observed hydride resonance (Fig. 5a and b). Moreover, a variable temperature proton NMR study has shown that these spectra are temperature-dependent. This very complex phenomenon is under further study and will be the subject of an independent publication.

Thus, here also, protonated complexes $[\text{HM}(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4]^+$ are fluxional.

When $A = \text{OCH}_3$ we have seen from the infrared results that the two carbonyl stretching frequencies are of different intensity suggesting either an opening of the CO—M—CO angle or a mixture of *cis* and *trans* isomers. Furthermore the hydride is equally coupled to the four phosphorus atoms. But by lowering the temperature of the sample we have only observed a broadening of the signals of protons and the exchange phenomenon seems quite rapid. Finally, examination of spectroscopic results from the point of view of structural information gives evidence as for $\text{TaH}(\text{CO})_2(\text{dmpe})_2$ complexes [10] of fluxional behaviour of the $[\text{HM}(\text{CO})_{6-n}(\text{PA}_3)_n]^+$ complexes in solution.

In conclusion, as was expected, our results have shown that protonation of $M(\text{CO})_{6-n}(\text{PA}_3)_n$ is strongly dependent on two factors: the degree of replacement of carbonyl groups and the basicity of the ligands. The influence of these two factors is particularly well illustrated by the behaviour of $M(\text{CO})_3(\text{PA}_3)_3$ complexes where the trisubstitution level is necessary to get protonated compounds and the basicity of the ligand strongly influences the stability of the protonated form in relation to the trifluoroacetic acid concentration.

Experimental

Infrared spectra were recorded on a Perkin—Elmer 225 and NMR spectra were obtained with a Varian A60A.

The $M(\text{CO})_{6-n}(\text{PA}_3)_n$ complexes were synthesized by methods described previously [11].

Protonation was performed either in pure trifluoroacetic acid or in a mixture of trifluoroacetic acid and methylene chloride. In the case of $M(\text{CO})_2[\text{P}(\text{CH}_3)_3]_4$ compounds it was possible to isolate the protonated compounds.

Preparation of $[HM(CO)_2[P(CH_3)_3]_4]^+PF_6^-$

We have used the procedure given by Green et al. to protonate (π -C₆H₆)-Mo(PA₃)₃ complexes [12].

To a solution of M(CO)₂[P(CH₃)₃]₄ in ethanol an excess of concentrated hydrochloric acid solution was added. The solution was stirred for 10 min and a few drops of saturated aqueous ammonium hexafluorophosphate were added. A yellow powder precipitated which was collected and washed with water and dried. The yield was about 80% in the two cases.

[HM_o(CO)₂[P(CH₃)₃]₄]⁺PF₆⁻; yellow powder; m.p. 171°C (dec.). Calcd.: C, 27.90; H, 6.15; F, 18.98. Found: C, 27.23; H, 6.16; F, 18.90%.

[HW(CO)₂[P(CH₃)₃]₄]⁺PF₆⁻; yellow powder; m.p. 210°C (dec.). Calcd.: C, 24.34; H, 5.36; F, 16.52. Found: C, 24.43; H, 5.33; F, 16.82%.

This method cannot be extended to P(OCH₃)₃ complexes which are decomposed by water.

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