Journal of Organometallic Chemistry, 182 (1979) 221—224

ORGANOMETALLIC COMPOUNDS OF VANADIUM(V), PHENYLALKOXYOXOVANADIUM DERIVATIVES

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(Received May 26th, 1979)

Summary

The phenylalkoxyoxovanadium derivatives $PhVO(Oi\text{-}Pr)_2$ and PhVOCl(Oi-Pr) have been prepared. Their IR, ^1H and ^{13}C NMR spectra are reported. Attempts to synthetize $PhVO(OCH_2CF_3)_2$ failed.

Introduction

The organometallic chemistry of vanadium(V) remains virtually unexplored: only $VO(CH_2SiMe_3)_3$ [1], $PhVOCl_2$ [2], $CH_3VO(OR)_2$ (with R = i-Pr, sec-Bu, t-Bu) [3,4] and, very recently, $Cp_2VO(Cl)$ [5] have been reported.

This may be attributed to the sensitivity of vanadium(V) towards reduction by the usual alkylating agents in common oxygenated solvents (ether, THF, etc). We now report the synthesis and isolation of two organometallic derivatives of vanadium(V), $PhVO(Oi\text{-}Pr)_2$ (I) and PhVOCl(Oi-Pr) (II), which have been characterised by ^1H and ^{13}C NMR and IR spectroscopy.

Results and discussion

Various aryl and alkyl organometallic compounds react with transition metal halides in inert solvents. With vanadium, the more powerful alkylating agents cause extensive reduction of all the vanadium to the divalent or metallic state and often lead to highly complex products. Attempts to prepare methylvanadium(V) oxides from $LiCH_3$ and $VOClL_2$ (L = Oi-Pr, NEt_2, acac, OCH_2CF_3 in n-pentane give either reductions or unstable products. Attempts to prepare $PhVO(Oi\text{-}Pr)_2$ (I) by action of Ph_2Hg on $VOCl(Oi\text{-}Pr)_2$ failed whereas PhLi gave (I). Ph_2Hg reacted with $VOCl_2(Oi\text{-}Pr)$ and $VOCl_3$ to give (II) and $PhVOCl_2$, respectively [2].

The phenylvanadium(V) compounds were synthesized according to the following scheme:

$$\mathrm{VOCl(Oi\text{-}Pr)_2 + PhLi} \xrightarrow{\text{n-pentane}} \underset{\mathrm{(I)}}{\mathrm{PhVO(Oi\text{-}Pr)_2}} \mathrm{+ LiCl} \qquad (1)$$

$$\mathrm{VOCl_2(Oi\text{-}Pr) + Ph_2Hg} \xrightarrow{\text{n-pentane}} \underset{\mathrm{(II)}}{\mathrm{PhVOCl(Oi\text{-}Pr)}} \mathrm{+ PhHgCl} \qquad (2)$$

The difference in the behaviour of the metal—chlorine bonds towards the mild reagent Ph_2Hg and the powerful reagent PhLi is probably due to the decreasing reactivity of $VOCl_{3-x}(OR)_x$ when x increases [6].

The products are unstable and decompose spontaneously: I in few weeks and II in few hours. In all cases, biphenyl and orthovanadate(V) are recovered. When Ph_2Hg was treated with $VOCl(OCH_2CF_3)_2$ under the conditions required for the formation of II, the expected $PhVO(OCH_2CF_3)_2$ could not be identified, and immediate decomposition occurred: $VO(OCH_2CF_3)_3$ was isolated and characterised (IR, ^1H NMR, analysis) by comparison with an authentic sample [7]. This decomposition was studied by Carrick [8] with $PhVOCl_2$, and quantitative yields of biphenyl and $VOCl_2$ were obtained, whereas in our work the presence of the vanadium(IV) was never detected: The ^1H NMR spectra of various samples of $PhVO(Oi\text{-}Pr)_2$ recorded during the course of one month, showed the disappearance of the phenyl resonance signals and the growth of the well resolved peaks of the light yellow $VO(Oi\text{-}Pr)_3$.

^1H NMR data for compounds I and II are listed in Table 1. The ^{13}C NMR data for I can be compared to those for the related compounds Cp_2TiPh_2 and $PhSn(CH_3)_3$ [9] (See Table 2; we were unable to distinguish C_3 and C_4 resonance in I. The IR spectra of I and II are very similar, and show characteristic absorption bands for the phenyl group at 1590, 1480, 740 and 700 cm^{-1}. Some other assignments are given in Table 3.

Experimental

General remarks

All experiments were carried out under nitrogen in Schlenk-type glassware.

TABLE 1

^1H NMR DATA FOR $PhVO(Oi\text{-}Pr)_2$, $PhVOCl(Oi\text{-}Pr)$ and A RELATED COMPOUND

Compound	Chemical shifts [a]		
	aromatic group δ(Ph)	alkoxy group $\delta(H_\alpha)$	$\delta(H_\beta)$
$PhVO(Oi\text{-}Pr)_2$ [b]	7.05—7.70	5.25	1.25
$PhVOCl(Oi\text{-}Pr)$ [c]	6.85—7.45	4.98	1.00
$CH_3VO(Oi\text{-}Pr)_2$ [d]		5.32	1.30

[a] In ppm downfield with respect to TMS as internal standard for $PhVO(Oi\text{-}Pr)_2$ and as external standard for $PhVOCl(Oi\text{-}Pr)$. [b] Relative intensity $Ph/CH/(CH_3)_2$: 5/2/12. [c] Relative intensity $Ph/CH/(CH_3)_2$: 5/1/6. [d] Ref. 3.

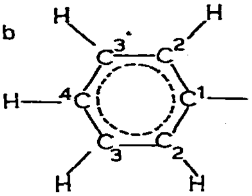
TABLE 2

^{13}C NMR DATA FOR $PhVO(Oi\text{-}Pr)_2$ AND RELATED COMPOUNDS [a]

Compound		Aromatic group [b]				Alkoxy group	
		C_1	C_2	C_3	C_4	C_α	C_β
$PhVO(Oi\text{-}Pr)_2$	$\delta\,^{13}C$	141.3	128.6		127.0	81.4	25.3
	$^1J_{C-H}$		155.9		154.4	125.0	141.2
	$^3J_{C-H}$		7.4				
$(CH_3)_3SnPh$	$\delta\,^{13}C$ [c]	141.6	135.6	128.0			
Cp_2TiPh_2	$\delta\,^{13}C$ [d]	192.9	136.0	127.3	124.3		

[a] δ in ppm downfield with respect to TMS as internal standard, coupling constant J in Hz.

b



[c] Ref. 9. [d] Ref. 10.

Solvents were dried over sodium wire before use. PhLi, $VOCl(Oi\text{-}Pr)_2$, $VOCl_2(Oi\text{-}Pr)$ and $VOCl(O\ CH_2CF_3)_2$ were prepared by published procedures [11,12,13,7].

Elemental analyses were performed by the Service de Microanalyse du C.N.R.S. IR spectra were recorded on a Perkin-Elmer 225 spectrophotometer as neat liquid between KBr plates. ^1H NMR spectra were recorded in C_6D_6 solution on a Perkin Elmer R 12 at 60 MHz and Fourier Transform ^{13}C NMR spectra on a Brucker WH 90 at 22.625 MHz.

Synthesis of $PhVO(Oi\text{-}Pr)_2$

$VOCl(Oi\text{-}Pr)_2$ (7.41 g, 34 mmol) in 50 cm^3 of n-pentane was stirred at —50° C and PhLi (2.99 g, 36 mmol) in n-pentane was added dropwise during 0.30 h. Stirring was continued for 3 h. The brown solution was filtered and the volatiles were removed under oxygen. The dark brown liquid was distilled to give $PhVO(Oi\text{-}Pr)_2$ as a yellow liquid (50° C/0.01 mmHg) in 20% yield. Anal.:

TABLE 3

IR DATA FOR $PhVO(Oi\text{-}Pr)_2$, $PhVOCl(Oi\text{-}Pr)$ AND RELATED COMPOUND

Compound	Main absorption bands (cm^{-1})			
	ν(V—Cl)	ν(V—C)	ν(V—O)	ν(V=O)
$PhVO(iO\text{-}Pr)_2$		545	660	1005
$PhVOCl(Oi\text{-}Pr)$	480	545	668	1015
$PhVOCl_2$ [a]	415s 508as	545		1038

[a] Ref. 2.

Found: C, 55.2; H, 7.9%; $C_{12}H_{19}O_3V$ Calcd.: C, 55.0; H, 7.3%. This liquid crystallized at room temperature (M.p 30° C).

Synthesis of PhVOCl(Oi-Pr)

A solution of $VOCl_2$(Oi-Pr) (5.21 g, 26 mmol) in 20 cm^3 of n-pentane was stirred at —10° C and a suspension of Ph_2Hg (10.19 g, 29 mmol) in 30 cm^3 of n-pentane was added during 0.30 h. Stirring was continued for 17 h. After filtration and evaporation of volatiles, the yellow liquid was purified by several crystallisations from n-pentane at —40° C to give PhVOCl(Oi-Pr).

The product is stable for only a few hours, even at low temperature.

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