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THE CHEMISTRY OF THE GROUP V METAL CARBONYLS V*. THE PREPARATION OF DERIVATIVES OF TETRACARBONYL-[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]VANADIUM(0)

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SUMMARY

Convenient synthesis of $HV(CO)_4[(C_6H_5)_2PCH_2]_2$, $IV(CO)_4[(C_6H_5)_2PCH_2]_2$, and $V(CO)_4[(C_6H_5)_2PCH_2]_2$ from $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ are described. The chemistry of the new hydrido and iodo derivatives is discussed in relationship to the parent carbonyl and other derivatives of vanadium hexacarbonyl.

INTRODUCTION

The convenient synthesis[1] of the $\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}^{-1}$ anion from $[V(CO)_6]^{-1}$ and 1,2-bis(diphenylphosphino)ethane has enabled us to explore the chemistry of this anion. Utilizing this species we were able to isolate the moderately stable seven-coordinate compounds $IV(CO)_4[(C_6H_5)_2PCH_2]_2$, and $HV(CO)_4[(C_6H_5)_2PCH_2]_2$. These are the first well characterized compounds of this type for which the neutral parent vanadium carbonyl is known***. The isolation of $HV(CO)_5(C_6H_5)_3P$ has been mentioned[3,4] but no supporting spectra, analyses or derivative chemistry are given to justify the formation. A poorly characterized compound, suggested[5] to be $IV(CO)_3$\{1,1,1-tris(diphenylphosphino)methyl]ethane\}, has been noted.

In this communication we discuss the relationship of the new hydrido and iodo derivatives to the systematic chemistry of $V(CO)_4[(C_6H_5)_2PCH_2]_2$.

EXPERIMENTAL

General procedures and starting materials

All operations were carried out under a nitrogen atmosphere with the precautions previously described[1]. The solvents were purified as described previously[1].

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* For Part IV see ref. 6.

** N.S.F. Traineeship 1970–71.

*** $HV(CO)_3$(mesitylene) and $IV(CO)_3$(mesitylene) have been prepared but the neutral parent carbonyl could not be prepared[2].

Methylene chloride was dried over and distilled from P_2O_5 and freed from oxygen by purging it with a dispersed stream of nitrogen.

With the exceptions noted below all other reagents were obtained from commercial sources and used without further purification.

(Triphenylstannyl)tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadium(0)[6], tetraethylammonium tetracarbonyl[1,2-bis(diphenylphosphino)ethane]-vanadate(–I)[1], tropylium tetrafluoroborate[7,8] and tetraphenylarsonium hydrogen dichloride[9] were prepared using the published procedures. The latter material was determined by titration to contain 92.5% available HCl in accord with the published results[10]. The silica gel used in the filtrations was column chromatography grade, 70–375 mesh (Merck).

Infrared spectra were recorded on a Perkin–Elmer Model 237B spectrometer. Melting points were determined on a Kofler hot stage microscope in sealed evacuated capillaries and are uncorrected. Elemental analyses were carried out by Spang Microanalytical Laboratory, Ann Arbor, Michigan and Mrs. N. F. Alvord of the M.I.T. Microanalytical Laboratory.

All reactions were monitored, in the metal carbonyl stretching frequency region, by infrared spectroscopy. When the bands corresponding to the carbonyl containing reactant disappeared or decreased to a constant intensity the reactions were stopped. All solvent evaporations and drying operations were done *in vacuo*, at or below room temperature.

Tetracarbonylhydrido[1,2-bis(diphenylphosphino)ethane]vanadium(I), $HV(CO)_4[(C_6H_5)_2PCH_2]_2$

(*a*). A suspension of 0.77 g (1.11 mmole) of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ was stirred at room temperature in 15 ml of tert-butyl chloride/heptane (2/1, v/v). Very little reaction occurred until water (15 ml) was added to the system. After $2\frac{1}{2}$ h the organic phase had become deep green and all of the reactant had been converted to a crystalline yellow solid which was insoluble in the aqueous phase and only very slightly soluble in the organic phase. The reaction mixture was cooled to 0° and the solid was separated via filtration at this temperature. It was then washed with 15 ml of water and dried. Finally, the material was washed with pentane (2 × 15 ml) and redried.

The resulting yellow microcrystalline solid (0.45 g, 71%) was analytically pure. It showed no definite decomposition point. Instead, it slowly turned green above 50°; above 130° the green color slowly gave way to an increasingly brown color. At 160° the solid was dark brown. (Found: C, 63.61; H, 4.41. $C_{30}H_{25}O_4P_2V$ calcd.: C, 64.07; H, 4.48%.)

The above product can be recrystallized from methylene chloride/heptane (8/1; v/v) at −20° to give yellow-brown crystals which show the same decomposition behavior on heating and also give satisfactory analyses. (Found: C, 63.57; H, 4.39%.)

(*b*). A benzene/heptane solvent mixture (40 ml; 8/1, v/v) was added to a mixture of 1.02 g (1.48 mmole) of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ and 0.730 g (1.48 mmole of HCl) of $[(C_6H_5)_4As][HCl_2]$. There was no immediate reaction. After stirring the slurry for $5\frac{1}{2}$ h at room temperature essentially all of the carbonyl anion had disappeared. The insoluble product was separated from the orange solution by filtration. Evaporation of the solvent from the filtrate at room temperature gave an oil which solidified *in vacuo*. The solid was then washed with cold (0°) pentane (2 x 10 ml) and dried at 0° to give a yield of 0.50 g (60%) of yellow microcrystalline solid. The solution and mull infrared spectra of this substance were identical to those of $HV(CO)_4[(C_6H_5)_2PCH_2]_2$ prepared above.

Reaction of tetracarbonylhydrido[1,2-bis(diphenylphosphino)ethane]vanadium(I) with tetraethylammonium hydroxide

A solution of 0.31 g (0.55 mmole) of $HV(CO)_4[(C_6H_5)_2PCH_2]_2$ in 15 ml of THF was stirred with 1.6 ml of a 10% aqueous solution (1.1 mmole) of $(C_2H_5)_4NOH$. Within a few seconds the THF solution began to turn red. The stirring was continued for 2 h. Subsequently the THF was evaporated. This left a suspension of orange red solid in the water. The solid was washed with additional water until the washings were nearly neutral. The dried solid (0.35 g; 91%) had a nujol mull infrared spectrum which was identical to that of genuine $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$.

Tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadium(0), $V(CO)_4[(C_6H_5)_2PCH_2]_2$

A slurry of 1.57 g (2.27 mmole) of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ and 0.40 g (2.27 mmole) of $[C_7H_7][BF_4]$ was stirred in benzene (50 ml) at room temperature. After 5 h the solution had become yellow green and all the carbonyl anion had been consumed. Evaporation of the filtered solution to dryness gave a deep green crystalline solid. This was washed with pentane (2 x 20 ml) and dried. A yield of 1.0 g (80%) of solid which smelled slightly of bitropyl was thereby obtained. A recrystallization from benzene/heptane (4/1; v/v) gave an analytically pure sample. Very slow evaporation of the above solution resulted in the formation of large deep green plates of product. The product became increasingly brown-yellow above 105°, slow frothing occurred above 140°C. No definite decomposition point was observed. (Found: C, 64.41; H, 4.38. $C_{30}H_{24}O_4P_2$ calcd.: C, 64.18; H, 4.31%.) The properties and spectra of this substance are identical to those previously reported[11].

Reduction of tetracarbonyl[1,2-bis(diphenylphosphino)ethane]vanadium(0) by sodium amalgam

A yellow solution of 0.173 g (0.31 mmole) of $V(CO)_4[(C_6H_5)_2PCH_2]_2$ in benzene (10 ml) was stirred with a 10-fold excess of 1% sodium amalgam. The solution rapidly changed to a red color. After the benzene solution had been stirred for 1 h it had become a pale orange color; much yellow solid had precipitated. The solution was then evaporated to dryness. The resulting solid was taken up in 15 ml of THF to give a red solution. The filtered solution was then evaporated to dryness. The crude solid was metathesized in ethanol (10 ml) with 0.12 g (0.62 mmole) of $(C_2H_5)_4NBr$. The solution was evaporated to dryness. The resulting impure solid was washed and triturated with water (3 x 10 ml), dried and recrystallized from 25 ml of acetone/heptane (4/1; v/v).

A yield of 0.130 g (61%) of orange-red crystalline solid was obtained. This gave solution and nujol mull infrared spectra which were identical to those found for genuine $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$.

Tetracarbonyliodo[1,2-bis(diphenylphosphino)ethane]vanadium(I), $IV(CO)_4[(C_6H_5)_2PCH_2]_2$

(*a*). Iodine (0.252 g, 0.99 mmole) in 10 ml of methylene chloride was added dropwise to a stirred slurry of 0.687 g (0.99 mmole) of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ in cold methylene chloride (20 ml at −40°). Within a few minutes after completion of the iodine addition the salt had dissolved completely. Although the solution became increasingly orange-brown on standing at −20° no new carbonyl containing species were detected by IR spectroscopy. In ½ h the methylene chloride was evaporated at −5°. An impure red brown substance was obtained. This was washed with pentane (2 × 15 ml) and dried. In an attempt to free the product of impurities it was dissolved in toluene (30 ml) at −10° and the resulting solution was filtered. The clear red-brown solution was then slowly evaporated at 0°. When all the solvent had been removed there remained a tarry red brown substance which was triturated and washed with pentane (2 × 15 ml) and dried. A yellow brown thermally unstable solid was thereby obtained (0.30 g, 44%). Attempts to purify the product further via fractional crystallization or column chromatography were not successful. The solid has no definite decomposition point. It slowly darkens. (Found: C, 51.46; H, 3.77. $C_{30}H_{24}IO_4P_2V$ calcd.: C, 52.35; H, 3.51%.)

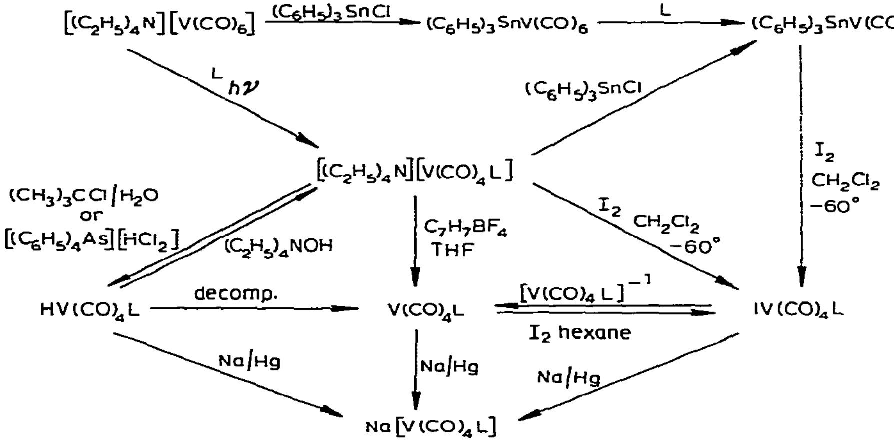
(*b*). It was also possible to prepare samples of $IV(CO)_4[(C_6H_5)_2PCH_2]_2$ by cleavage of $(C_6H_5)_3SnV(CO)_4[(C_6H_5)_2PCH_2]_2$ with an equivalent of I_2, at low temperature (−60°), in methylene chloride. By cautiously concentrating the solution at −20° and adding a large excess of cold (ca. −50°) pentane it was possible to obtain bright yellow orange precipitates of $IV(CO)_4[(C_6H_5)_2PCH_2]_2$.

RESULTS AND DISCUSSION

The hydride $HV(CO)_4[(C_6H_5)_2PCH_2]_2$ is obtained in good yield either by the acidification of $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ with $[(C_6H_5)_4As][HCl_2]$ in benzene or by the interaction of this carbonyl metallate with tert-butyl chloride in the presence of water. The reagent $[(C_6H_5)_4As][HCl_2]$ was found to be a particularly convenient air and vacuum stable strong acid. However, the reaction with tert-butyl chloride was more easily carried out. The yellow neutral hydride is moderately air stable and can be exposed to air briefly, unlike the parent carbonyl $V(CO)_4[(C_6H_5)_2PCH_2]_2$ which is very air sensitive. The solid hydride is stable under nitrogen at −10°. However, at room temperature it slowly decomposes to the black-green $V(CO)_4[(C_6H_5)_2PCH_2]$ (ca. 2 weeks). Solutions of the hydride deteriorate to the paramagnetic parent carbonyl much more rapidly. This latter reaction has prevented the observation of an NMR signal for the hydride proton. The hydride can be cleanly transformed into salts of $\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}^{-1}$ either by reduction with 1% sodium amalgam or by neutralization with aqueous tetraethylammonium hydroxide in THF. The latter reaction establishes the presence of one acidic hydride in the molecule; $V(CO)_4[(C_6H_5)_2PCH_2]_2$ does not interact with $(C_2H_5)_4NOH$ under these conditions. Similarly the isolation of $[(C_2H_5)_3NH]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ from acetonitrile solutions of the hydride and triethylamine is further confirmation of the presence of an acidic hydrogen.

The neutral paramagnetic complex $V(CO)_4[(C_6H_5)_2PCH_2]_2$, which has been reported[11] previously from the reaction of $V(CO)_6$ and 1,2-bis(diphenylphosphino)ethane, can be obtained either from decomposition of the hydride or more conveniently can be synthesized in high yield from the interaction of $[C_7H_7][BF_4]$ with $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$. It is more solvolytically stable than $V(CO)_6$, SCHEME 1

PREPARATION AND INTERCONVERSIONS OF VARIOUS DERIVATIVES OF TETRACARBONYL[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]VANADIUM(0)



L = 1,2-bis(diphenylphosphino)ethane.

e.g. it persists in THF at room temperature for at least an hour without any sign of decomposition; whereas $V(CO)_6$ rapidly disproportionates under these conditions. The neutral carbonyl can be reduced to $\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}^{-1}$ by % sodium amalgam in THF. This behavior contrasts with that of all previously reported reductions of substituted vanadium carbonyls, namely, *trans*-$V(CO)_4[(C_6H_5)_3P]_2$[12] and *cis*-$V(CO)_4$ $[RCH{=}CHCH_2P(C_6H_5)_2]$[13], which undergo ill understood ligand redistribution reactions to give $[V(CO)_5L]^{-1}$ anions.

The neutral carbonyl, $V(CO)_4[(C_6H_5)_2PCH_2]_2$, has also been prepared in attempts to obtain mixed transition metal carbonyl species from $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ and metal carbonyl halides, *e.g.* equivalent amounts of $BrMn(CO)_5$ and $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ gave good yields of $Mn_2(CO)_{10}$ and $V(CO)_4[(C_6H_5)_2PCH_2]_2$.

The iodo complex, $IV(CO)_4[(C_6H_5)_2PCH_2]_2$, has been prepared by four independent routes. Although we initially prepared the complex by the cleavage of the Sn–V bond in $(C_6H_5)_3SnV(CO)_4[(C_6H_5)_2PCH_2]_2$ by iodine in methylene chloride at −60°, it can be most readily prepared from the interaction of iodine with $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ under the same conditions. Similarly, it results from the reaction of the latter salt with C_2F_5I. It can, however, also be prepared from the reaction of $V(CO)_4[(C_6H_5)_2PCH_2]_2$ with the stoichiometric amount of iodine in hexane.

The chemical properties of $IV(CO)_4[(C_6H_5)_2PCH_2]_2$ are consistent with its formulation. Reduction of this substance by 1% sodium amalgam gives $\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}^{-1}$ in good yield. It also undergoes a redox reaction with $[(C_2H_5)_4N]\{V(CO)_4[(C_6H_5)_2PCH_2]_2\}$ to give $V(CO)_4[(C_6H_5)_2PCH_2]_2$ quantitatively.

The infrared spectra (Table 1) of $HV(CO)_4[(C_6H_5)_2PCH_2]_2$, $IV(CO)_4[(C_6H_5)_2PCH_2]_2$, and $V(CO)_4[(C_6H_5)_2PCH_2]_2$ are similar in the carbonyl stretching frequency region and as expected the bands for the iodo complex are shifted to

TABLE 1

INFRARED SOLUTION AND MULL SPECTRA IN THE CARBONYL REGION

Complex	Medium	C–O stretching frequencies (cm^{-1})[a]
$IV(CO)_4[(C_6H_5)_2PCH_2]_2$	CH_2Cl_2	2016 s, 1957 s, 1911 vs, 1880 s
	Nujol Mull	2008 s, 1943 vs, 1905 vs(b), 1869 vs(b)
$HV(CO)_4[(C_6H_5)_2PCH_2]_2$	CH_2Cl_2	1998 s, 1879 vs(b)
	Nujol Mull	1988 m, 1890 vs, 1867 vs(sh), 1856 vs
$V(CO)_4[(C_6H_5)_2PCH_2]_2$	CH_2Cl_2	1995 vs, 1895 s(sh), 1876 vs(sh), 1860 vs(b)
	Nujol Mull	1985 s, 1889 s, 1870 vs, 1849 vs

[a] s=strong; m=medium; v=very; sh=shoulder; b=broad.

higher energies compared to the corresponding bands in the other two complexes.

The mull spectrum of the neutral carbonyl is sufficiently similar to that of the hydride that small amounts of one in the other are difficult to detect. However, because the carbonyl band of the hydride at highest energy is less intense than the corresponding and nearly superimposable band in the neutral carbonyl, the growth of the latter substance in samples of $HV(CO)_4[(C_6H_5)_2PCH_2]_2$ can be conveniently monitored by the increase in intensity of the composite band.

Studies on the reactions of $\{M(CO)_4[(C_6H_5)_2PCH_2]_2\}^{-1}$, M=Nb and Ta, are in progress. However, the behavior is markedly different from that reported here for the vanadium systems.

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