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THE REACTIONS OF VANADIUM HEXACARBONYL WITH OLEFIN-PHOSPHINE LIGANDS

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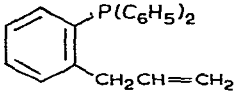
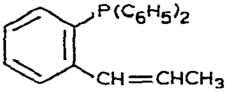
SUMMARY

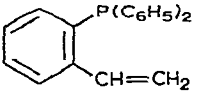
Monoolefin complexes of vanadium(0) of the type $LV(CO)_4$ have been prepared using the bidentate ligands (2-allylphenyl)diphenylphosphine and (2-*cis*-propenylphenyl)diphenylphosphine. Upon reduction these yield the vanadium(−I) complexes, $R^+[LV(CO)_5]^-$, in which the olefin-phosphine ligands are coordinated only through the phosphorus atom. Information regarding the mode of coordination of the ligands, and the metal–olefin interaction in the case of the $LV(CO)_4$ complexes, is obtained from infrared spectral data and is discussed in the context of previous studies of olefin-phosphine complexes.

INTRODUCTION

The ability of the olefin-substituted triphenylphosphine derivatives shown below to serve as bidentate, chelating ligands toward a variety of transition metals has been well documented[1].


AP=(2-allylphenyl)-
diphenylphosphine


PP=(2-*cis*-propenyl-
phenyl)diphenylphosphine


SP=*o*-styryl-
diphenylphosphine

Through the use of these ligands, the range of metals which form stable monoolefin complexes has been extended and new information regarding the metal–olefin interaction has been obtained. For example, an infrared spectral study of a homologous series of metal–olefin complexes including both Group VI $\{[LM(CO)_4]$; L=PP or SP; M=Cr, Mo or W$\}$[1a,c] and Group VII $\{[LM(CO)_4^+]Y^-$; L=AP, PP or SP; M=Mn or Re$\}$[1f] metal derivatives has revealed a dependence in the C=C stretching frequency [ν(C=C)] upon the metal and its formal charge. The trends in

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{$\Delta\nu$(C=C)} observed, *i.e.* W > Cr > Mo, Re^+ > Mn^+, Cr > Mn^+, and W > Re^+, were interpreted in terms of a predominately π-acceptor role for the olefin in these complexes. Efforts to extend this homologous series to include the isoelectronic vanadium(−I) derivatives, $R^+[LV(CO)_4^-]$ have resulted in the investigation of the interaction of vanadium hexacarbonyl with these ligands reported herein.

The chemistry of $V(CO)_6$ exhibits the following features. In addition to the usual CO substitution reactions, under certain conditions $V(CO)_6$ undergoes disproportionation to yield derivatives of $V(CO)_6^-$. This is particularly true for hard bases such as triphenylphosphine oxide, pyridine-*N*-oxide and amines, which give products of the type: $(VB_n)^{2+}$ $[V(CO)_6^-]_2$[2]. With soft bases, such as phosphines and arsines, simple substitution products of vanadium(0) can be obtained; however, even in these cases the use of certain solvents for the reaction, such as ethers, can lead to disproportionation[2–4]. Also, the substitution products isolated in the absence of disproportionation often show some tendency toward dimerization with postulated pairing of the odd electron on vanadium (0) through metal–metal bonding. For example, whereas triphenylphosphine gives simple monomeric and paramagnetic substitution products, tricyclohexylphosphine yields a (presumably) metal–metal bonded dimer[3].

The reaction with bidentate ligands such as bis(diphenylphosphino)ethane (DP)[5] and *o*-phenylene-bis(dimethylarsine)[6] can result in either simple monomeric substitution products, metal–metal bonded dimers or disproportionation, depending upon the ligand and the conditions of the reaction. Although the reaction of $V(CO)_6$ with aromatic hydrocarbons has been studied[7] apparently no olefin-complexes of vanadium (0) have been previously reported.

EXPERIMENTAL

The ligands used in this study, AP and *cis*-PP, were prepared by previously described procedures[1a,f] and carefully purified before use by repeated sublimation until free of phosphine oxides, as judged by the absence of the P=O stretching vibration in the infrared at 1000–1100 cm^{-1}. Without this purification the reactions with $V(CO)_6$ gave impure products which contained the $V(CO)_6^-$ anion. Bis(diglyme)sodium hexacarbonyl vanadate(−I) was obtained from Strem Chemicals and 100% orthophosphoric acid from Matheson, Coleman and Bell. All reactions involving $V(CO)_6$ were carried out either *in vacuo* or under an atmosphere of prepurified nitrogen carefully dried and deaerated solvents.

Vanadium hexacarbonyl

This compound was prepared by a modification of the procedure suggested by Werner[8] which utilizes the following reaction:

$$[Na(diglyme)_2][V(CO)_6] + H_3PO_4 \rightarrow V(CO)_6 + 0.5\,H_2 + NaH_2PO_4 + 2\text{diglyme}$$

diglyme = diethyleneglycol dimethyl ether

Bis(diglyme)sodium hexacarbonyl vanadate(−I) (2.5 g) was mixed under nitrogen with enough 100% orthophosphoric acid crystals to thoroughly cover the yellow salt in a 100 ml round-bottom flask. The flask was connected in series with two traps.

The first trap contained P_2O_5 and was cooled with a chlorobenzene slush bath (−42.5°). The second was cooled with dry ice/acetone and was connected to vacuum. The reaction flask was then evacuated and the blue-green $V(CO)_6$ generated was collected in the P_2O_5 trap. The diglyme of solvation which is freed passes through the P_2O_5 trap and was removed by warming the dry ice/acetone cooled trap. When the blue color had disappeared from the reaction flask, the P_2O_5 was allowed to warm up, moving the $V(CO)_6$ to the dry ice/acetone cooled trap. The whole apparatus was then filled with dry nitrogen and removed to a nitrogen-filled dry box where the $V(CO)_6$ receiver was removed, capped and weighed (0.998 g; 95%). In general, due to the instability of $V(CO)_6$, the material was used the same day as prepared.

The identity and purity of the $V(CO)_6$ prepared was checked by condensing a small amount of the material from one preparation into a 10 cm gas cell with KBr windows. The infrared spectrum of the vapor taken with the sample cooled in ice consisted of only one broad absorption band at 1989 cm^{-1}, close to the value previously reported for the infrared active CO stretching vibration of $V(CO)_6$[9].

Preparation of the LV(CO)$_4$ complexes (L = AP, cis-PP)[4]

Vanadium hexacarbonyl (1.346 g; 6.15 mmole) was dissolved in 75 ml hexane under nitrogen with stirring. After cooling the solution to 0°, 1.855 g (6.15 mmole) of AP (or *cis*-PP) in 50 ml hexane was added dropwise over 2 h with stirring. After stirring for an additional 5 h at 0° a total of 10.70 mmole of CO was collected. The hexane was then removed under reduced pressure through a trap at −78° which retains any unreacted $V(CO)_6$ (0.082 g; 0.38 mmole). The evolved CO amounted to 1.86 mmole CO/mmole $V(CO)_6$ reacted. The yellow-brown solid remaining was rinsed with 50 ml absolute ethanol under N_2 to yield 2.498 g (87.3%) of an extremely air-sensitive yellow-green solid, which darkened upon prolonged exposure to light. A sample of this material (0.235 g; 0.506 mmole) in a pyrex tube was attached to the vacuum line connected to a Toepler pump. Excess iodine condensed into the tube evolved 1.985 mmoles of CO from the sample upon heating, [3.92 mole/mole (AP)V(CO)$_4$]. Two other samples were analyzed for vanadium by volumetric iodide/iodate[10]. (Found: V, 11.0 (average value). $C_{25}H_{19}O_4PV$ calcd.: V, 10.94%.) (*Cis*-PP)V(CO)$_4$, prepared by the same method, was identified by its infrared spectrum. Both solids decomposed upon solution in carbon tetrachloride, chloroform, benzene, ethyl ether, and tetrahydrofuran (THF), and were insoluble in water and ethanol.

Reduction of the LV(CO)$_4$ complexes[4]

An excess of freshly prepared 1% sodium amalgam (ca. 50 g) was added to the products of the preceding reaction along with 30–40 ml of degassed ethanol. The mixture was stirred vigorously for 0.5 h at room temperature under nitrogen yielding a reddish-brown solution. The supernatant solution was decanted, leaving the excess mercury and amalgam behind. After filtering, the reddish-brown solution was treated dropwise with a stoichiometric amount of either tetramethylammonium iodide or tetra-n-propylammonium iodide dissolved in 4–5 ml of deareated water. A yellow precipitate forms, which was filtered, dried *in vacuo*, rinsed with 75 ml n-pentane and then recrystallized from THF/ether. Yields of 0.7 to 2.1 g (ca. 80%) were obtained. The material is soluble in acetone, ethanol, and THF, slightly soluble in ethyl ether and water, insoluble in hydrocarbons and decomposes in acetonitrile. The solid is relatively stable in air for a few hours, stable for 3–4 days under nitrogen, and stable longer if protected from light. In solution the material can be handled without decomposition only under scrupulously oxygen-free conditions and must be kept away from light. Reactions of $V(CO)_6$ with 2 moles of ligand under the conditions described above for the $LV(CO)_4$ complex preparation followed immediately by reduction gave identical $R^+[L_{uo}V(CO)_5^-]$[*] complexes. Attempts to reduce the $LV(CO)_4$ complexes by reaction with tetrakis(dimethylamino)ethylene[11] at room temperature in ethanol, ether, THF and benzene resulted in immediate decomposition of the $LV(CO)_4$ complexes. Similarly efforts to displace CO by the olefin in the $R^+[L_{uo}V(CO)_5^-]$ complexes by heating in refluxing ethanol led to decomposition of the starting complexes. The direct reaction of $Na(diglyme)_2^+ V(CO)_6^-$ with the ligands was also attempted in diglyme solution but no evidence for substitution was obtained after heating for 50 h at 95°.

Measurements

Infrared spectra were obtained in the solid state as Nujol and hexachlorobutadiene mulls using a Perkin–Elmer Model 421 IR spectrophotometer. The mulls were all prepared in a nitrogen filled drybox. The magnetic susceptibility of the $(AP)V(CO)_4$ complex was determined at room temperature by the Gouy method. The complex was packed into a tared Gouy tube in a nitrogen filled drybox and the tube tightly sealed to prevent air oxidation during the measurement. The tube was calibrated with $HgCo(SCN)_4$ and a diamagnetic correction applied to the measurements using Pascal's constants[12]. The measured susceptiblity χ_M at 20° was 1412×10^{-6} cgs units; χ_M (corr.) $= 1652 \times 10^{-6}$ cgs units; μ (corr.) (20°) = 1.98 BM. Elemental analysis of the $[N(alkyl)_4^+][L_{uo}V(CO)_5^-]$ complexes were performed by the microanalytical laboratory of the University of California and are reported in Table 1.

RESULTS AND DISCUSSION

The olefin-phosphine derivatives of vanadium hexacarbonyl were prepared by direct reaction of equimolar amounts of the starting materials in hexane solution

TABLE 1

ANALYTICAL DATA FOR THE $[N(alkyl)_4][L_{uo}V(CO)_5]$ COMPLEXES

Alkyl	L_{uo}	Analysis found (calcd.) (%)			
		C	H	N	P
Methyl	AP	62.95	5.39	2.52	5.36
		(63.50)	(5.51)	(2.42)	(5.46)
n-Propyl	AP	66.60	7.05	2.01	4.45
		(67.15)	(6.97)	(2.06)	(4.56)
Methyl	*cis*-PP	63.05	5.42	2.47	5.40
		(63.50)	(5.51)	(2.42)	(5.46)
n-Propyl	*cis*-PP	66.82	7.15	2.01	4.39
		(67.15)	(6.97)	(2.06)	(4.56)

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[*] L_{uo} = monodentate *cis*-PP or AP ligand.

TABLE 2

C–O STRETCHING FREQUENCIES FOR THE $LV(CO)_4$ COMPLEXES

Complex	Frequencies (cm^{-1})[a]			
$(AP)V(CO)_4$	2005 ms	1932 ms	1912 s	1861 vs
$(cis\text{-}PP)V(CO)_4$	2001 ms	1924 ms	1910 s	1849 vs
$(DP)V(CO)_4$[b]	1985 ms	1888 ms	1870 s	1847 vs

[a] Determined as Nujol mulls. [b] Ref. 5; determined as KBr pellet.

at 0°. In the course of this reaction, two moles of carbon monoxide were released for each mole of $V(CO)_6$ reacted, suggesting that the CO is displaced by one mole of bidentate ligand to give compounds of the empirical formula $LV(CO)_4$ (L=*cis*-PP, AP). Additional support for this formulation was provided by vanadium analysis and measurement of the CO released upon oxidation of the AP complex with I_2. The spectra obtained for these complexes in the CO stretching region of the infrared (Table 2) are consistent with a *cis*-disubstituted octahedral structure and closely resemble the CO spectrum of $V(CO)_4(DP)$*[,5], which molecular weight measurements indicate to be monomeric. Also, the observation of a room temperature magnetic moment of 1.98 BM for the $(AP)V(CO)_4$ complex indicates that, like $V(CO)_4(DP)$, these complexes are paramagnetic with one unpaired electron per vanadium. The instability of these complexes in solution and their sensitivity to light and heat have precluded molecular weight determinations; however, it appears likely on the basis of the foregoing data that they are indeed simple monomeric substitution products of $V(CO)_6$.

The infrared spectra of the $LV(CO)_4$ complexes (Table 3) also yields information regarding the nature of the olefin-phosphine ligands coordinated to vanadium. First of all it is apparent that the (2-allylphenyl)diphenylphosphine ligand has not undergone isomerization to the *cis*-propenyl isomer as was observed in the case of the Group VI metal derivatives[1a]. Instead, like all of the other transition metals except for the Group VI series which have been studied thus far, vanadium gives distinctly different AP and *cis*-PP complexes, both of which exhibit spectral features characteristic of the respective parent ligands.

Additional evidence for coordination of the olefin portion of the ligands in these complexes was also provided by the infrared spectra. As was observed earlier for chelated olefin-phosphine complexes[1], the band attributed to the C=C stretching frequency of the free olefin is replaced in the spectra of the vanadium complexes by a new band in the 1480–1580 cm^{-1} region, which is assigned to the C=C stretching vibration of the coordinated olefin (Fig. 1). The shift in C=C stretching frequency $\Delta\nu(C{=}C)$ is 126 cm^{-1} for the *cis*-PP vanadium complex and 124 cm^{-1} for the AP derivative. These values are in approximately the same range as those previously obtained for the $LCr(CO)_4$ (L=*cis*-PP, SP)[1a] derivatives (119–120 cm^{-1}) indicating a metal–olefin interaction of comparable magnitude for these two metals.

Upon reduction of the $LV(CO)_4$ complexes with sodium amalgam, anionic vanadium(–I) derivatives were obtained which were isolated as their NMe_4^+ and NPr_4^+ salts. Elemental analyses and infrared spectral data show that CO substitution

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* DP=bis(diphenylphosphino)ethane.

TABLE 3

INFRARED DATA FOR THE OLEFIN-PHOSPHINE LIGANDS AND THEIR METAL COMPLEXES (1700–650 cm^{-1})

Assignment	AP and its complexes				*Cis*-PP and its complexes			
	L^a	$[L_{uo}V(CO)_5]^{-b}$	$LPtBr_2$ [a]	$LV(CO)_4$	L^a	$[L_{uo}V(CO)_5]^{-b}$	$LCr(CO)_4$ [a]	$LV(CO)_4$
C=C str.	1637 w	1637 w	1492 (sh)	1513 vw	1644 vw	1642 vw	1525 vw (br)	1518 vw (br)
Arom. ring str.	1587 w	1587 w	1587 w	1587 w	1582 w	1582 w	1582 w	1590 w
	1563 vw	1563 vw	1570 vw	1568 vw			1567 vw (br)	1570 vw
	1478 w	1478 w	1482 w	1478 w	1479 w	1479 w	1484 w	1481 w
Aliph. C–H def.	1464 w	1470 w	1471 w		1460 w	1461 w	1462 w	1466 w
	1435 m	1433 m	1435 m	1438 m	1435 m	1437 m	1435 m	1430 m
Arom. and olef. C–H in-plane def.	1406 (sh)	1385 m	1383 vw	1395 vw	1397 vw	1398 vw	1391 w	1398 w
	1323 (sh)	1321 m	1326 vw	1328 vw	1364 w	1364 w	1364 w	1362 w
	1307 vw	1309 mw	1305 vw	1309 vw	1325 vw	1325 vw	1326 vw	1327 vw
	1087 w	1086 w	1092 m	1092 m	1307 vw	1306 vw	1305 vw	1299 vw
	1027 w	1031 w	1020 mw	1022 vw	1091 w (br)	1091 w	1095 m	1085 m
					1025 mw	1025 m	1034 mw	1027 vw
Arom. and olef. C–H out-of-plane def.	908 m	909 m			927 w	928 w	907 w (br)	918 w
			765 m	766 w	814 mw	814 mw	817 w	824 w
				759 s				806 w
	748 s	747 s	750 s	750 s	767 ms	767 ms	761 m	764 m
			711 w	717 w	743 ms	743 ms	748 ms	743 ms
	696 s	692 s	700 vs	696 vw			704 ms	702 ms
			688 s	676 m	694 s	694 s	693 ms	689 ms
				664 s			664 s	664 s

[a] Ref. 1a. [b] Bands associated with the $N(n\text{-}Pr)_4^+$ cation were also observed at 1076 m, 957 m, 741 m and 680 m cm^{-1}.

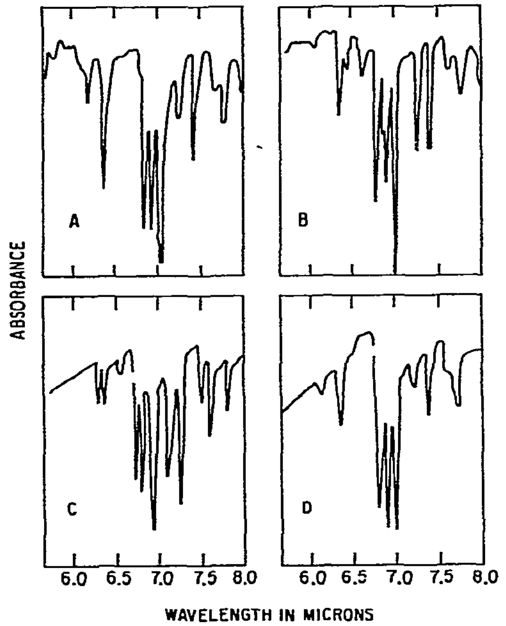

Fig. 1. Infrared spectra of (2-*cis*-propenylphenyl)diphenylphosphine (*cis*-PP) and its complexes: A. *cis*-PP in deuteriochloroform solution[1a]; B. (*cis*-PP)Cr$(CO)_4$ in deuteriochloroform[1a]; C. (*cis*-PP)V$(CO)_4$ in Nujol (ca. 5.5–6.7 μm) and in hexachlorobutadiene (6.7–8.0 μm) mulls; D. $[(cis\text{-PP})_{uo}V(CO)_5]^-$ as the NPr_4^+ salt in Nujol (ca. 5.5–6.7 μm) and in hexachlorobutadiene (6.8–8.0 μm) mulls.

accompanies this reduction leading to octahedral complexes of the type $R^+[L_{uo}V(CO)_5]^-$. In contrast to the $LV(CO)_4$ complexes, the infrared spectra of the $R^+[L_{uo}V(CO)_5]^-$ derivatives in the 1480–1650 cm^{-1} region are essentially identical with the free ligand spectra in this region, showing no indication of metal–olefin interaction.

The spectrum observed in the CO stretching region (Table 4), although not very typical of $DM(CO)_5$ complexes, can be understood on that basis. Under C_{4v} symmetry three infrared active absorption bands would be expected for a $DM(CO)_5$ complex, corresponding to the E and $2A_1$ stretching modes[13]. However, the asymmetry of the phosphine substituent in this case reduces the overall molecular symmetry such that all CO stretching moles are theoretically infrared active and non-degenerate. Coupled with the additional symmetry reducing effect of the solid state environment of these complexes, the observation of five absorption bands is not at all unreasonable. It is noteworthy that the spectrum of the corresponding $R^+[(C_6H_5)_3PV(CO)_5]^-$

TABLE 4

C–O STRETCHING FREQUENCIES FOR THE $[L_{uo}V(CO)_5]^-$ ANIONS

L_{uo}	Frequencies (cm^{-1})[a]				
AP	1970 m	1868 s	1820 s	1788 s	1768 s (br)
cis-PP	1970 m	1864 s	1818 s	1786 s	1768 s (br)
PPh_3[b]	1953 m	1842 s (br)	1805 s	1767 s (br)	

[a] Determined in the solid state as Nujol mulls. [b] Determined as KBr pellet[2].

derivative (Table 4)[4] is only one step removed from this situation, exhibiting four absorption bands in the same frequency range as those of the $R^+[L_{uo}V(CO)_5]^-$ complexes.

The incorporation of CO under similar conditions has been observed for the bis(triphenylphosphine) complex, $[(C_6H_5)_3P]_2V(CO)_4$, which yields the $(C_6H_5)_3PV(CO)_5^-$ anion upon reduction with Na/Hg in either ethanol or benzene[3,4]. Therefore, it is likely that the source of the CO in these cases is the starting vanadium(0) complex. The occurrence of this ligand displacement by CO seems to reflect a strong tendency on the part of the vanadium(−I) ion to surround itself with ligands of high π-acceptor capability.

The ability of the olefin-phosphines to behave as monodentate as well as bidentate ligands has also been evidenced previously with several other transition metals[1d,e], however, for metal carbonyl derivatives[1a,c,f] only bidentate coordination has hitherto been observed. Attempts to prepare the chelated $LV(CO)_4^-$ complexes by other means, including direct reaction of the ligands with $V(CO)_6^-$ salts, reduction of the $LV(CO)_4$ complexes with tetrakis(dimethylamino)ethylene and heating the $R^+[LV(CO)_5]^-$ derivatives in solution, have been unsuccessful, leading either to decomposition of the starting complexes or else no reaction.

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