Journal of Organometallic Chemistry, 220 (1981) 45—54
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

THE COORDINATIVE PROPERTIES OF THE LIGANDS $Ph_2ECH_2EPh_2$ (E = P, As, Sb) IN CARBONYLVANADIUM COMPLEXES, AND THE MOLECULAR STRUCTURE OF η^5-$C_5H_5V(CO)_3As_2Ph_4$

RENATE BOROWSKI, DIETER REHDER * and KLAUS VON DEUTEN

Institut für Anorganische und Angewandte Chemie der Universität, Martin-Luther-King-Platz 6, D 2-Hamburg 13 (F.R.G.)

(Received May 8th, 1981)

Summary

Photo-reaction between the ligands $Ph_2ECH_2EPh_2$ (E = P: dppm, E = As: dpam, E = Sb: dpsm), L, and the vanadium complexes η^5-$C_5H_5V(CO)_4$ and $[Et_4N][V(CO)_6]$ yields monosubstituted mononuclear (dpsm) and dinuclear, ligand-bridged complexes (dpam, dpsm). With dppm, the final products are disubstituted chelate complexes, but monosubstituted mono- and dinuclear species are formed as intermediates.

The shielding of the ^{51}V nucleus decreases in the series dpsm > dppm > dpam and $\{M(CO)_n\} > \{M(CO)_{n-1}\}L > \{M(CO)_{n-1}\}_2\mu$-L $> \{M(CO)_{n-2}\}$dppm ($\{M(CO)_n\} = [V(CO)_6]^-$, η^5-$C_5H_5V(CO)_4$). The half-widths of the NMR signals are greater for dinuclear than for mononuclear complexes.

The crystal and molecular structures of η^5-$C_5H_5V(CO)_3As_2Ph_4$ have been determined. The compound crystallizes in the space group $P2_1/c$ with $a = 1347.8$, $b = 1020.0$, $c = 2085.2$ pm and $\beta = 82.3°$. Due to steric crowding, the ^{51}V shielding is low compared to that of $\{\eta^5$-$C_5H_5V(CO)_3\}_2\mu$-dpam.

Introduction

Oligodentate ligands containing phosphorus, arsenic and antimony functions usually react with carbonylvanadium complexes to form monometallic monoligate chelate complexes [1,2,3], except where the steric conditions favour the formation of ligand-bridged dinuclear species. Thus, E_2R_4 (E = P, R = Me, Cy, Ph; E = As, Sb, R = Ph) [4], p-$C_6H_4(PPh_2)_2$ [5] and *trans*-$Ph_2PCH{=}CHPPh_2$ [6], L, afford complexes of the type $\{M\}_2\mu$-L ($\{M\} = CpV(CO)_3$, $V(CO)_5^-$). With the bidentate ligands $Ph_2As(CH_2)_2PPh_2$ (arphos) and $Ph_2As(CH_2)_2AsPh_2$(dpae), L′, the complexes $[\{V(CO)_5\}_2\mu$-L′$]^{2-}$ are obtained; they are rather stable towards further CO substitution and can be converted into the mononuclear *cis*-$[V(CO)_4L']$ only by UV irradiation for several hours [7].

0022-328X/81/0000—0000/$02.50

We have shown earlier that $Ph_2PCH_2PPh_2$ (dppm) forms chelate complexes with $[V(CO)_6]^-$ and $CpV(CO)_4$ [1]. The low shielding of the ^{51}V nucleus in these complexes indicates considerable distortions in the 4-ring structure [1,8]. The reinvestigation described in this paper shows that the reaction path is more complex than previously assumed. We have also extended our investigations to the corresponding arsenic and antimony ligands, $Ph_2AsCH_2AsPh_2$ (dpam) and $Ph_2SbCH_2SbPh_2$ (dpsm). The coordination properties of the three ligands are of interest in the light of the varying spatial requirement of the donor/acceptor functions and their differing ligand strengths and nephelauxetic effects [2,9]. The ligands dppm, dpam and dpsm thus provide suitable systems for distinguishing between the factors (steric or electronic) dominating their coordination to vanadium. Since the shielding of the ^{51}V nucleus is a very sensitive indicator of variations of electronic and steric effects upon the character of the vanadium—ligand bond [8], we mainly interpret our results on the basis of ^{51}V NMR measurements. In this context, we have also determined the X-ray structure of $CpV(CO)_3As_2Ph_4$; this complex exhibits by far the lowest ^{51}V shielding observed for monosubstituted $CpV(CO)_4$ derivatives containing arsenic ligands.

Results and discussion

$CpV(CO)_3As_2Ph_4$

Crystals of $CpV(CO)_3As_2Ph_4$ [4] were grown by allowing a ca. 0.1 *M* solution of the complex in 1/2 toluene/heptane to stand at 0°C for three weeks. The crystals were prepared under nitrogen. The compound crystallizes in the space group $P2_1/c$ with $a = 1347.8$, $b = 1020.0$, $c = 2085.2$ pm and $\beta = 82.3°$ ($V = 2840.5 \times 10^6$ pm^3, $Z = 4$). Structural data are listed in Tables 1 and 2. Figure 1 shows an ORTEP drawing of the molecule.

The V—As bond length (253.6 pm) is slightly longer than, e.g., that in η^3-$C_3H_4MeV(CO)_3o$-$C_6H_4(AsMe_2)_2$ (averaged value: 250.7 pm [10]). The

TABLE 1

SELECTED STRUCTURAL DATA FOR η^5-$C_5H_5V(CO)_3As_2Ph_4$

Bond distances (pm)		Bond angles (°)	
V—C(1)	228.1(0.9)	V—C(6)—O(6)	172.9(0.6)
V—C(2)	228.2(0.8)	V—C(7)—O(7)	177.6(0.6)
V—C(3)	226.7(0.9)	V—C(8)—O(8)	176.5(0.6)
V—C(4)	223.0(0.9)	C(6)—V—C(7)	74.3(0.3)
V—C(5)	223.4(0.9)	C(7)—V—C(8)	75.6(0.3)
V—C(6)	191.8(0.7)	C(6)—V—As(1)	81.5(0.2)
V—C(7)	186.3(0.7)	C(8)—V—As(1)	76.8(0.2)
V—C(8)	193.0(0.7)	V—As(1)—As(2)	111.9(0.0)
V—As(1)	253.6(0.1)	V—As(1)—C(111)	112.9(0.2)
As(1)—As(2)	247.2(0.1)	V—As(1)—C(121)	119.0(0.2)
C(6)—O(6)	115.4(0.8)	C(111)—As(1)—C(121)	103.3(0.3)
C(7)—O(7)	118.5(0.9)	C(111)—As(1)—As(2)	100.7(0.2)
C(8)—O(8)	114.7(0.9)	C(121)—As(1)—As(2)	107.2(0.2)
As(1)—C(111)	191.5(0.8)	As(1)—As(2)—C(211)	97.2(0.2)
As(1)—C(121)	193.4(0.7)	As(1)—As(2)—C(221)	107.9(0.2)
As(2)—C(211)	192.0(0.7)	C(211)—As(2)—C(221)	103.2(0.3)
As(2)—C(221)	196.0(0.8)		

(Continued on p. 49)

TABLE 2

FRACTIONAL COORDINATES AND THERMAL FACTORS (X10^4)

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
V	1570(1)	—3470(1)	3624(1)	370(7)	333(8)	454(7)	—12(6)	—21(6)	—42(6)
C(1)	380(6)	—3314(10)	4508(5)	499(60)	652(78)	510(72)	—169(67)	64(54)	—188(61)
C(2)	—103(6)	—3281(10)	3971(5)	467(57)	500(71)	800(73)	24(60)	59(52)	54(55)
C(3)	65(6)	—4473(10)	3651(5)	417(57)	740(84)	578(69)	105(69)	—56(52)	—245(53)
C(4)	691(7)	—5222(9)	4004(5)	581(65)	282(68)	765(74)	—3(63)	—55(52)	—174(55)
C(5)	900(6)	—4494(9)	4527(4)	499(59)	418(66)	645(71)	80(57)	—90(51)	—52(50)
C(6)	1520(5)	—2028(7)	3039(3)	512(50)	525(58)	312(49)	—87(41)	—38(40)	—213(44)
C(7)	1897(5)	—4170(7)	2797(4)	465(51)	407(51)	584(56)	71(46)	—80(46)	—44(40)
C(8)	2847(5)	—4315(7)	3647(3)	554(55)	427(52)	43(46)	—151(41)	—14(44)	—47(45)
C(111)	2974(6)	—2492(6)	4970(3)	639(61)	267(44)	318(51)	—18(38)	107(48)	—103(44)
C(112)	3982(7)	—2917(8)	4877(4)	725(75)	485(57)	478(64)	75(51)	—187(60)	—58(52)
C(113)	4252(9)	—3482(9)	5528(6)	921(102)	513(66)	884(89)	28(65)	—485(85)	—90(67)
C(114)	3593(12)	—3659(9)	6061(5)	1690(130)	442(65)	537(84)	105(62)	—596(94)	—195(78)
C(115)	2605(10)	—3243(9)	6067(5)	1288(102)	462(64)	642(84)	—137(64)	—143(84)	—46(70)
C(116)	2350(7)	—2681(7)	5510(5)	835(80)	329(53)	518(66)	27(46)	—213(66)	36(51)
C(211)	1369(6)	910(7)	3852(3)	328(52)	365(49)	612(57)	—86(43)	—28(49)	—49(42)
C(212)	418(7)	1047(8)	3674(5)	676(79)	425(56)	613(68)	—22(50)	—128(62)	—87(54)
C(213)	273(9)	1703(11)	3114(6)	937(100)	589(71)	1030(103)	—55(68)	—568(88)	33(75)
C(214)	1063(11)	2222(9)	2725(5)	1427(125)	495(69)	559(82)	—3(59)	—382(89)	27(75)
C(215)	2006(10)	2089(9)	2885(5)	924(98)	570(69)	670(82)	76(61)	—96(77)	21(66)
C(216)	2120(7)	1429(8)	3450(5)	617(84)	462(60)	625(71)	—14(49)	—264(66)	122(59)
C(121)	3739(5)	—1041(7)	3741(4)	467(51)	448(53)	331(50)	—2(43)	43(43)	112(44)
C(112)	3883(6)	—1251(9)	3114(5)	300(57)	932(77)	718(76)	14(64)	—48(52)	—242(53)
C(123)	4782(8)	—640(13)	2753(5)	498(74)	1602(114)	736(90)	184(87)	—111(71)	—221(69)
C(124)	5340(8)	250(12)	3044(6)	608(81)	1257(110)	972(91)	531(97)	49(83)	—139(74)
C(125)	5104(8)	459(10)	3678(8)	502(79)	612(79)	1525(138)	44(93)	—307(86)	—223(59)
C(126)	4304(6)	—161(8)	4066(4)	434(54)	511(57)	651(62)	—96(55)	20(53)	—43(47)
C(221)	2279(5)	1205(7)	5103(4)	554(50)	310(53)	330(51)	—117(42)	—28(41)	128(41)
C(222)	2502(6)	2474(8)	4876(4)	805(65)	467(62)	3906(57)	18(55)	—160(50)	—47(49)
C(223)	2957(7)	3330(9)	5262(5)	988(72)	450(66)	695(72)	118(69)	—348(57)	—45(60)
C(224)	3197(7)	2926(10)	5828(5)	968(77)	536(84)	818(89)	—179(68)	—424(66)	—82(59)
C(225)	2959(7)	1696(11)	6066(4)	1176(80)	601(75)	551(70)	—47(70)	—331(61—	327(65)

TABLE 2 (continued)

Atom	x/a	Y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(226)	2504(6)	833(8)	5683(4)	936(69)	402(59)	394(61)	—47(54)	—153(50)	—20(54)
O(6)	1454(4)	—1252(5)	2644(2)	967(42)	469(37)	480(36)	51(29)	—186(32)	—71(32)
O(7)	2108(4)	—4570(5)	2263(2)	727(38)	714(42)	596(35)	—143(33)	—56(31)	77(31)
O(8)	3581(4)	—4877(5)	3660(3)	628(39)	805(43)	983(44)	—75(38)	—113(35)	333(37)
As(1)	2536(0)	—1808(1)	4200(0)	367(4)	335(4)	409(4)	6(64)	—27(3)	—23(4)
As(2)	1457(1)	18(1)	4654(07)	447(4)	389(4)	523(5)	—1(5)	—27(4)	19(5)
					Atom	x/a	y/b	z/c	U_{11}
H(1)	356(41)	—2847(54)	4833(25)	288(237)	H(215)	2515(49)	2317(66)	2597(32)	675(327)
H(2)	—414(44)	—2578(59)	3832(29)	423(258)	H(216)	2675(32)	1455(50)	3549(24)	1(184)
H(3)	—42(42)	—4654(61)	3214(27)	664(247)	H(122)	3642(42)	—1841(57)	2901(27)	298(230)
H(4)	859(40)	—6019(50)	3813(26)	268(219)	H(123)	4926(52)	—812(70)	2300(31)	824(312)
H(5)	1197(35)	—4836(53)	4897(23)	430(188)	H(124)	5989(54)	646(71)	2717(34)	1100(314)
H(112)	4433(31)	—2721(41)	4582(21)	1(147)	H(125)	5366(42)	825(54)	3906(28)	145(210)
H(113)	4887(52)	—3707(76)	5472(34)	738(381)	H(126)	4109(36)	30(53)	4569(25)	389(177)
H(114)	3726(45)	—3971(60)	6461(30)	595(258)	H(222)	2458(38)	2795(51)	4426(25)	408(211)
H(115)	2167(48)	—3422(72)	6473(32)	735(322)	H(223)	3131(46)	4122(62)	5029(30)	662(261)
H(116)	1673(41)	—2401(53)	5472(26)	480(233)	H(224)	3412(43)	3398(61)	6112(28)	407(247)
H(212)	—156(39)	740(51)	3980(24)	322(204)	H(225)	2993(39)	1431(56)	6500(26)	440(214)
H(213)	—268(45)	1664(74)	2989(32)	713(295)	H(226)	2245(44)	—96(62)	5861(29)	753(247)
H(214)	1026(52)	2550(64)	2316(33)	883(326)					

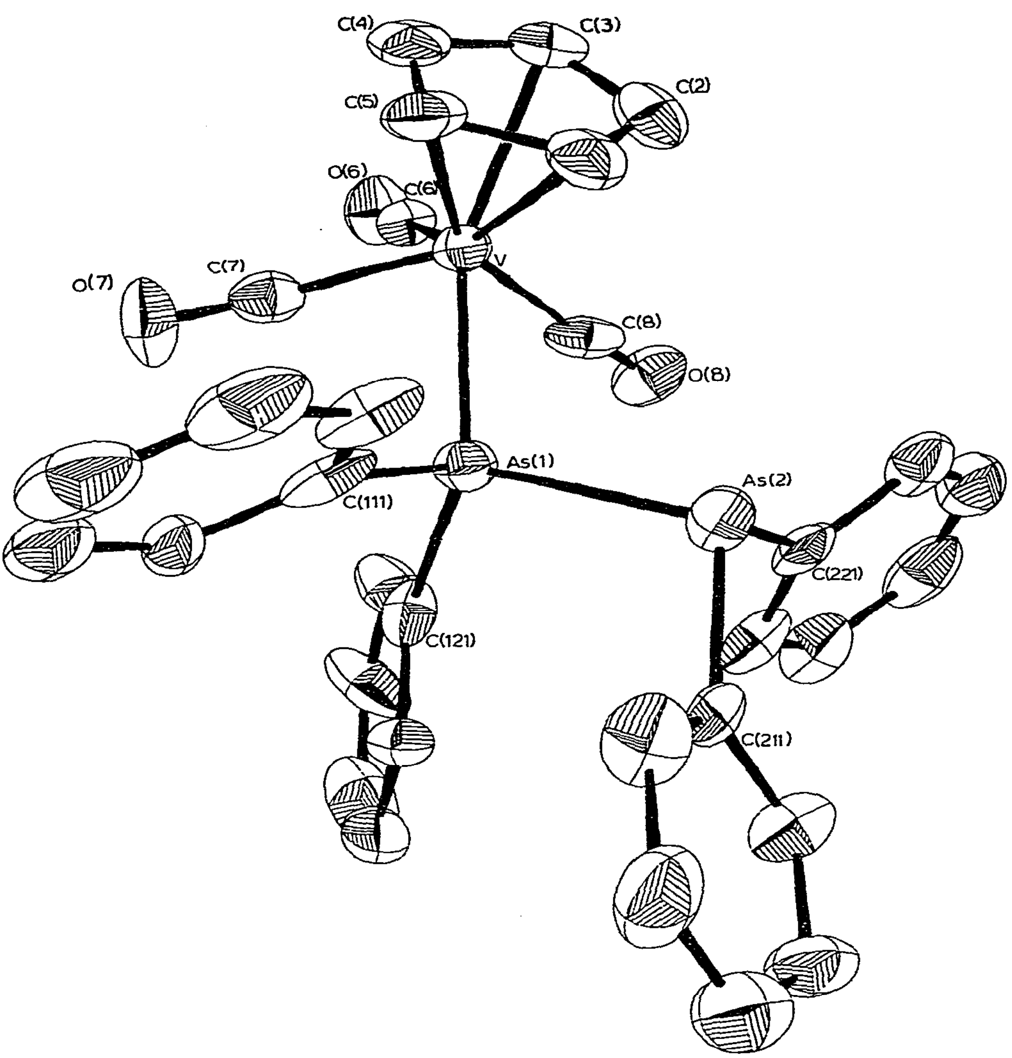

Fig. 1. ORTEP drawing and numbering of atoms for η^5-$C_5H_5V(CO)_3(C_6H_5)_2AsAs(C_6H_5)_2$. Hydrogen atoms are omitted for clarity.

angles at the vanadium atom compare to those found in other derivatives of $CpV(CO)_4$ ([$CpV(CO)PhP(CH_2CH_2PPh_2)_2$: 76.8° [11], $CpV(CO)_2Ph_2P(CH_2)_2PPh_2$: 79.0° [12]) and, concerning the other bond parameters, there are no significant differences between $CpV(CO)_3As_2Ph_4$ and comparable vanadium complexes (see listing in ref. 13). This result is somewhat embarassing in the light of the consistently low ^{51}V shielding ($|\delta| = 1145$ ppm; compare $CpV(CO)_3AsPh_3$ and $\{CpV(CO)_3\}_2\mu$-dpam: 1260 ppm) and the greater half width $\Delta\nu_{1/2}$ (344 as compared to 213 and 235 Hz).

We have shown earlier that there is a close relationship between $|\delta|$ and the ligand bulk in as much as $|\delta|$ decreases with increasing steric requirement of the ligand due to decreasing metal—ligand interaction and increasing paramagnetic deshielding of the metal nucleus [8]. Further, line widths are expected to increase with increasing bulk of the molecule, an effect which reflects slower reorientation, i.e. diminished relaxation times for large molecules. Thus, while the greater steric requirement of As_2Ph_4 as compared to $AsPh_3$ and dpam is consistent with the ^{51}V NMR parameters of the complexes, it is not parallelled by significant deviations of the V—As bond length and angles at the vanadium center. At present, this inconsistency cannot easily be accounted for.

Complexes with dppm, dpam and dpsm

IR and ^{51}V NMR data are contained in Table 3. For comparison improved spectral parameters of a few known complexes are included.

All the complexes were prepared by irradiation of approximately 0.01 *M* THF solutions of the ligands and the parent carbonyl complexes. The product spectrum is independent of the molar ratio of reactants. In solution, the compounds are highly sensitive to oxygen. They are isolated by precipitation with heptane and form orange to wine-red powders (dppm, dpam) or dark red oils (dpsm). The well-dried solids can be exposed to air several minutes without decomposition.

The reactions between dpam and $CpV(CO)_4$ or $[V(CO)_6]^-$, yield the dinuclear, ligand-bridged complexes only. The spectral parameters are practically identical to those of the mononuclear $AsPh_3$ complexes, but $|\delta|$ for $[\{V(CO)_5\}_2\mu\text{-dpam}]^{2-}$ is slightly less than that of $[\{V(CO)_5\}_2\mu\text{-dpae}]^{2-}$, and $|\delta|\{CpV(CO)_3\}_2\mu$-dpam exceeds $|\delta|CpV(CO)_3As_2Ph_4$ by ca. 100 ppm (see above). These variations may reflect the increasing bulk of the ligands in the order dpae <

TABLE 3

^{51}V NMR AND IR DATA

Complex [a]	Ref.	$\delta(^{51}V)$ (ppm) [b] $[^1J(PV)$ (Hz)]	$\Delta\nu_{1/2}$ (Hz) [c]	$\nu(CO)$ (cm^{-1}) [d]
$CpV(CO)_3$dppm, 1	e	−1340 [195] [f]	f	1950, 1872
$\{CpV(CO)_3\}_2\mu$-dppm, 2	e	−1299.5	444 [g]	
$CpV(CO)_3PPh_2Me$	8	−1368 [150]		1950, (1863), 1850
cis-$[CpV(CO)_2$dppm], 3	e	−860	540 [g]	1871, 1808
$[V(CO)_5PPh_2Me]^-$	8	−1839 [200]	75(2)	1963, 1859, 1818
cis-$[V(CO)_4\text{dppm}]^-$, 4	e	−1598 [190]	144(7)	1901, 1800, 1780, 1743
$\{CpV(CO)_3\}_2\mu$-dpam, 5	e	−1260.1	235(4)	1958, (1875), 1866
$CpV(CO)_3AsPh_3$	e	−1258.8	213(2.5)	1954, (1856), 1856
$CpV(CO)_3As_2Ph_4$	e	−1145.2	344(5)	1955, 1870, 1859
cis-$[CpV(CO)_2$dpae]	7	−937		1870, 1800
$[\{V(CO)_5\}_2\mu\text{-dpam}]^{2-}$, 6	e	−1805.4	274(3)	1866, 1859, 1832, (1790)
$[\{V(CO)_5\}_2\mu\text{-dpae}]^{2-}$	7	−1824		1965, 1858, 1825
cis-$[V(CO)_4\text{dpae}]^-$	7	−1754		1895, (1792), 1780, 1755
$CpV(CO)_3$dpsm, 7a	e	−1398.5	504(11)	1950, 1876, 1852
$\{CpV(CO)_3\}_2\mu$-dpsm, 7b	e	−1368.0	658(16)	
$CpV(CO)_3SbPh_3$	e	−1429.7	153(7)	1949, 1871, 1851
$[\{V(CO)_5\}_2\mu\text{-dpsm}]^{2-}$, 8	e	−1875.3	437(7)	1967, 1862, 1833, (1810)
$[V(CO)_5SbPh_3]^-$	e	−1881.4	388(5)	1968, 1859, 1832

[a] dppm = $Ph_2PCH_2PPh_2$, dpam = $Ph_2AsCH_2AsPh_2$, dpsm = $Ph_2SbCH_2SbPh_2$, dpae = $Ph_2AsCH_2CH_2AsPh_2$. [b] Relative $VOCl_3$, 300 ± 1 K, ca. 0.1 *M* THF. Coupling constants in square brackets. [c] Half widths of the ^{51}V NMR signals. Absolute error in brackets. [d] Ca. 0.01 *M* THF. Bands in brackets are estimated positions (shoulders). [e] This work. [f] Resolution incomplete (see Fig. 2). [g] Scalar + quadrupolar broadening.

dpam ~ $AsPh_3 < As_2Ph_4$ (see also the discussion in the previous section). The ligand dpam does not form chelate complexes; its coordination behaviour thus differs from that of dppm and dpae (which give chelate rings because of lower steric hindrance).

The reaction between dpsm and $[V(CO)_6]^-$ parallels that for dpam, but with $CpV(CO)_4$ a mixture of mono- and dinuclear species is obtained; this can be separated by several recrystallizations from heptane/toluene [$\{CpV(CO)_3\}_2\mu$-dpsm is more soluble in heptane than $CpV(CO)_3$dpsm]. The two species are easily distinguished by their ^{51}V chemical shifts (whereas they exhibit identical IR patterns in the CO stretching region). The consistent decrease of the ^{51}V shielding in the series $SbPh_3$ > dpsm > μ-dpsm again demonstrates the steric influence upon δ.

To account for the different behaviour of dpsm in the reactions with $CpV(CO)_4$ and $[V(CO)_6]^-$, respectively, it can be assumed that the large antimony species impart a photo-chemical instability with respect to the V—Sb bond in the case of the $CpV(CO)_4$ derivatives, where, in the dinuclear form, two sterically unfavourable tetragonal pyramidal $\{CpV(CO)_3SbPh_2\}$ units are linked via the methylene group. The formation of the dinuclear complex is then counteracted by the competing back-reaction to the mononuclear complex. We have observed similar competing steps in the reaction between $CpV(CO)_4$ and o-$C_6H_4(AsPh_2)SbPh_2$ (asb), where the vanadium—ligand bond in *cis*-[$CpV(CO)_2$asb] is labilized to the extent that considerable amounts of $CpV(CO)_3$asb are present regardless of the irradiation times [5].

The photo-induced introduction of dppm into $CpV(CO)_4$ gives further insight into the reaction path. Depending on the irradiation time, $CpV(CO)_3$dppm, $\{CpV(CO)_3\}_2\mu$-dppm and *cis*-[$CpV(CO)_2$dppm] are formed successively. Figure 2 illustrates the product spectrum after ca. half an hour of irradiation under

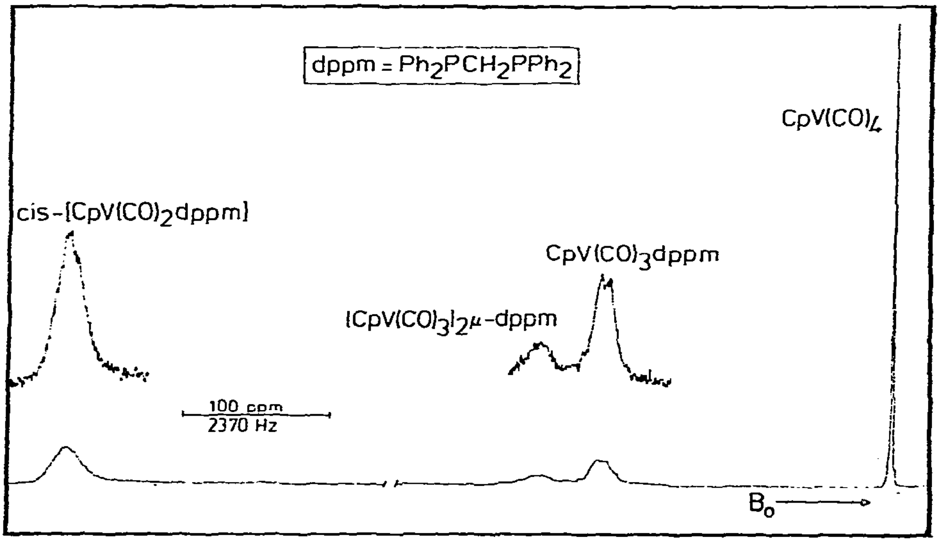

Fig. 2. The 23.66 MHz ^{51}V NMR spectrum of a reaction mixture obtained by irradiation of η^5-$C_5H_5V(CO)_4/Ph_2PCH_2PPh_2$ (0.1 *M* THF) for 0.5 h.

standard conditions. The line widths of the ^{51}V NMR signals increase, $|\delta|$ decrease in the series $CpV(CO)_4 > CpV(CO)_3PPh_2Me > CpV(CO)_3dppm > \{CpV(CO)_3\}_2\mu$-dppm > *cis*-$[CpV(CO)_2dppm]$. With $[V(CO)_6]^-$, only the chelate complex *cis*-$[V(CO)_4dppm]$ can be isolated (see also ref. 1). Shielding in this complex is lower than in *cis*-$[V(CO)_4(PPh_2Me)_2]^-$, because of perturbation of the V—P overlap caused by strains in the chelate 4-ring [8].

Although steric hindrance results in a decrease in $|\delta|$, the ^{51}V shielding of the complexes containing the extremely bulky antimony ligands is higher than that for the phosphorus complexes, i.e. dpsm > dppm > dpam (the same ordering was observed for $SbPh_3$, $AsPh_3$, PPh_3 [2] and *o*-phenylene ligands carrying the groups $SbPh_2$, $AsPh_2$ and PPh_2 [5]). Hence, an electronic effect has to be taken into account. We suggest that for the ordering of Sb and P ligands the large nephelauxetic effect of the stibines overrides effects arising from other contributions to the overall shielding, while the positions of P and As ligands reflect the greater ligand strength (π-acceptor power and σ-donor ability) of phosphines [2,5,8].

Experimental

General methods and materials

The apparatus used for the photo-reactions was described previously [14]. All operations were carried out in oxygen-free solvents under nitrogen.

$CpV(CO)_4$ and $[Na(diglyme)_2][V(CO)_6]$ were purchased (Strem), the latter was converted to $[Et_4N][V(CO)_6]$ by a reported procedure [1]. The preparation of the ligands from CH_2Cl_2 and $NaEPh_2$ (E = P, As, Sb) in liquid ammonia was carried out by procedures analogous to the procedure given by Sato et al. [15] (see also refs. 16—18). For the preparation of the dppm complexes see ref. 1; for $CpV(CO)_3As_2Ph_4$ see ref. 4.

X-ray structure determination

A total of 2667 independent reflections was collected with the help of the θ—2θ technique on a Hilger & Watts diffractometer (Mo-K_α, graphite monochromator). Anisotropic full matrix least squares refinement for 2491 significant ($F_0 > 3\sigma_{F_0}$) reflections lead to a final weighted R-value of 0.027. All computations employed the SHEL 76 program system [19].

Spectroscopic measurements

IR: ca. 0.02 M THF solutions in 0.1 mm KBr cuvettes, Perkin Elmer spectrometer 337. ^{51}V NMR: ca 0.1 M THF solutions in 7.5 mm diameter vials fitted into rotating 10 mm vials containing acetone-d_6 as external lock; Bruker WH 90 spectrometer, 23.66 MHz, 300 ± 1 K, average number of scans ca. 1000. The spectra were digitalized and fitted by a least squares procedure, using the program NMRFIT [20]. The absolute error of the chemical shifts thus obtained is less than 0.1 ppm (the error, however, due to temperature variations of ±1 degree is 0.5 ppm; the concentration dependence of the shift is negligable); for the absolute error of the half widths see Table 3.

Procedures

$\{\eta^5\text{-}C_5H_5V(CO)_3\}_2\mu\text{-}(C_6H_5)_2AsCH_2As(C_6H_5)_2$ *(5).* 374 mg $CpV(CO)_4$ (1.64 mmol) and 388 mg dpam (0.82 mmol) were dissolved in 50 ml THF and irradiated for 30 min, during which the solution changed from orange to red and dark-brown. After concentration to ca 5 ml (room temperature, ca. 1 Torr), the solution was treated slowly with 15 ml n-heptane with vigorous stirring. A fine powder was precipitated, and after standing at 0°C overnight, this was filtered off, washed twice with n-heptane/THF, 4/1, and dried under high vacuum (6 hours). 550 mg (72% yield) of brick-red **5** were thus obtained. Found: C, 56.6; H, 4.0; As, 16.6; V, 11.4. $C_{41}H_{32}As_2O_6V_2$ (872.4) calcd.: C, 56.44; H, 3.70; As, 17.18; V, 11.68%.

$[(C_2H_5)_4N]_2[\{V(CO)_5\}_2\mu\text{-}(C_6H_5)_2AsCH_2As(C_6H_5)_2]$ *(6).* 30 ml of a THF solution containing 315 mg $[Et_4N][V(CO)_6]$ (0.9 mmol) and 213 mg dpam (0.45 mmol) were irradiated for 90 min. The darked-brown solution was concentrated to ca. 5 ml and treated dropwise with ca. 15 ml of n-heptane with vigorous stirring (in order to avoid formation of pasty products). A brown, powdery precipitate was obtained, and after standing at 0°C overnight, this was filtered off and dissolved in 5 ml THF/toluene, 1/1. The solution was filtered and the solid reprecipitated with heptane. The yellow-brown precipitate was dried under high vacuum. Yield 220 mg (42%). Found: C, 55.5; H, 5.7; N, 2.4; As, 12.8; V, 8.8. $C_{51}H_{62}As_2N_2O_{10}V_2$ (1114.8) calcd.: C, 54.95; H, 5.61; N, 2.51; As, 13.44; V, 9.14%.

$\eta^5\text{-}C_5H_5V(CO)_3(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$ *(7a) and* $\{\eta^5\text{-}C_5H_5V(CO)_3\}_2\mu\text{-}(C_6H_5)_2SbCH_2(C_6H_5)_2$ *(7b).* A mixture of 590 mg $CpV(CO)_4$ (2.6 mmol) and 754 mg dpsm (1.3 mmol) in 50 ml THF was irradiated for 100 min. The dark solution was then concentrated to ca 5 ml, and a dark-red, viscous oil (**7a** + **7b**) was precipitated by addition of 15 ml n-heptane. The red supernatant solution (**7a**, **7b** and $CpV(CO)_4$) was decanged and the oil was dried in vacuo.

Ca. 300 mg of this oil were dissolved in 5 ml toluene and ca. 80 ml heptane were added with vigorous stirring. On standing at 0°C for several days, a dark red oil (enriched in **7a**) separated out. Almost pure **7b** was isolated from the motherliquor as a viscous, red oil by removal of the solvents at room temperature and ca. 1 Torr.

$[(C_2H_5)_4N]_2[\{V(CO)_5\}_2\mu\text{-}(C_6H_5)SbCH_2Sb(C_6H_5)_2]$ *(8).* This complex was prepared as described for **6**, except that the irradiation apparatus described in ref. 3 with an internal UV source in a quartz immersion well was used. The irradiation time for 100 ml of a THF solution containing 625 mg $[Et_4N][V(CO)_6]$ (1.8 mmol) and 508 mg dpsm (0.9 mmol) was 165 min. The complex was isolated as a dark-red oil (Yield: 45%).

References

1 D. Rehder, L. Dahlenburg, and I. Müller, J. Organometal. Chem., 122 (1976) 53.
2 R. Talay and D. Rehder, Z. Naturforsch., 366 (1981) 451.
3 D. Rehder and U. Puttfarcken, J. Organometal. Chem., 184 (1980) 343.
4 H. Baumgarten, H. Johannsen, and D. Rehder, Chem. Ber., 112 (1979) 2650.
5 R. Talay and D. Rehder, unpublished work.
6 H.-Ch. Bechthold and D. Rehder, J. Organometal. Chem., 172 (1979) 331.

7 W. Roose, D. Rehder, H. Lüders, and K.H. Theopold, J. Organometal. Chem., 157 (1978) 321.
8 D. Rehder, J. Magn. Reson., 38 (1980) 419.
9 R. Talay and D. Rehder, Chem. Ber., 111 (1978) 1978.
10 U. Franke and E. Weiss, J. Organometal. Chem., 168 (1979) 311.
11 K. von Deuten, and D. Rehder, W. Roose, J. Organometal. Chem., 214 (1981) 71.
12 D. Rehder, I. Müller, and J. Kopf, J. Inrog. Nucl. Chem., 40 (1978) 1013.
13 T. Greiser, U. Puttfarcken, and D. Rehder, Trans. Met. Chem., 4 (1979) 168.
14 H.-Ch. Bechthold and D. Rehder, J. Organometal. Chem., 206 (1981) 305.
15 S. Sato, Y. Matsumara, and R. Okawara, J. Organometal. Chem., 43 (1972) 333.
16 W. Levason, C.A. McAuliffe, and S.G. Murray, J. Organometal. Chem., 88 (1975) 171.
17 W. Hewertson and H.R. Watson, J. Chem. Soc., (1962) 1490.
18 T. Yoshida, M. Iwamoto, and S. Yuguchi, Japan lat., 11, 934 ('67); see Chem. Abstr., 68 (1968) 105358.
19 G. Sheldrick, Program for Crystal Structure Determination, Cambridge, England 1975.
20 G. Fricke, Technische Hochschule Darmstadt (F.R.G.), Laborbericht 27; revised version by K. Paulsen, Hamburg 1980.