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CARBONYLHYDRIDOPHOSPHINEVANADIUM COMPLEXES. A NOVEL ROUTE TO HYDRIDO COMPLEXES BY ION EXCHANGE ON SILICA GEL

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Summary

The hydrido complexes $HV(CO)_4\widehat{PP}$, where $\widehat{PP}$ = [illegible] $HV(CO)_4(Ph_2AsCH_2CH_2PPh_2)$, and $HV(CO)_3$ [illegible] were prepared by treatment of the corresponding [illegible] vanadates(−I) with silica gel. The compounds were characterized by [illegible] and ^{51}V NMR spectra.

Introduction

[illegible]

[illegible]

TABLE 1

SPECTROSCOPIC DATA FOR CARBONYLHYDRIDOPHOSPHINEVANADIUM COMPLEXES

	$\delta(^{51}V)$ [a] (ppm)	$\Delta\nu_{1/2}$ [b] (Hz)	$\delta(^{1}H)$ [c] (ppm)	$^{2}J(^{1}H—^{31}P)$ (Hz)	$\nu(C{\equiv}O)$ [e] (cm^{-1})			
I	—1593	708	—5.04(t)	21.9	1989m	1901(sh)	1878s	1857(sh)
II	—1690	720	—5.03(t)	26.0	1990s	1878vs(br)		
III	—1600	695	—4.91(t)	25.9	1990s	1909w	1867vs	1831w
IV	—1553	700	—5.15(t)	26.7	1988s	1895w	1867s	1839m
V	—1663	718	—5.08(d)	25.9	1990s	1875vs(br)		
VI	—1640	915	—4.54 [d]	20, 39 [d]	1927(sh)	1920s	1835(sh)	1820s

[a] Ca. 0.1 *M* THF. Standard: $VOCl_3/CDCl_3$ 2/1 external. The chemical shift values are between those of carbonylvanadates(—I) and carbonylvanadium(+I) compounds (cf. ref. 9). [b] Half-width of the ^{51}V resonance signal. [c] In THF-d_8 at 295 K (I—V) and 333 K (VI), respectively. [d] Six lines are observed (intensity ratio 1/1/2/2/1/1); $^{2}J(H—PPh_2)$ 39 Hz, $^{2}J(H—PPh)$ 20 Hz; $\Delta\nu_{1/2}$ 5 Hz (at 333 K). See also Fig. 1. [e] Ca. 0.02 *M* THF.

Results and discussion

Starting from the complex anions *cis*-$[V(CO)_4\widehat{PP}]^-$ ($\widehat{PP}$ = bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$), which can be prepared by photoinduced reaction between $[Et_4N][V(CO)_6]$ and $\widehat{PP}$ [9], we describe here an unconventional and convenient method for the preparation of the hydrido complexes $HV(CO)_4\widehat{PP}$ on silica gel carriers (n = 1, dppm (I); n = 2, dppe (II); n = 3, dppp (III); n = 4, dppb (IV)). Yields are about 70%. The reaction can also be applied to *cis*-$[V(CO)_4arphos]^-$ (arphos = $Ph_2AsCH_2CH_2PPh_2$) [10] and *cis*-$[V(CO)_4triphos]^-$ (triphos = $Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2$) [11], resulting in the formation of $HV(CO)_4arphos$ (V) and $HV(CO)_3triphos$ (VI) *, respectively. IR, ^1H NMR and ^{51}V NMR spectroscopic data of the complexes I—VI are compiled in Table 1.

The reaction is possibly initiated by ion exchange processes due to the potentially acid {Si—OH}-groups (eq. 1).

$$cis\text{-}[Et_4N][V(CO)_4\widehat{PP}] + \{H^+\} \rightleftharpoons HV(CO)_4\widehat{PP} + \{Et_4N^+\} \qquad (1)$$

Using a convenient eluant such as THF (I, II, V), THF/heptane mixtures (III, IV), or THF/toluene (VI), the hydrido complex is drawn off by successive chromatography on silica gel. Elimination of CO with simultaneous formation of chelated structures according to eq. 2 and 3 may occur when a free phosphorus

$$\{H^+\} + [V(CO)_5\widehat{PP}]^- \rightarrow HV(CO)_4\widehat{PP} + \{CO\} \qquad (2)$$

$$\{H^+\} + cis\text{-}[V(CO)_4triphos]^- \rightarrow HV(CO)_3triphos + \{CO\} \qquad (3)$$

function is available in the starting anion.

The solutions thus obtained are sensitive to oxygen. Addition of n-heptane precipitates the complexes I—VI as micro-crystalline, yellow powders which change to ochre (II—VI) or dark-brown (I) within a few days, though this is not accompanied by any observable change in their spectroscopic properties.

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* Recently, we described this complex as $\{fac\text{-}[V(CO)_3triphos]\}_2$ (cf. ref. 11).

TABLE 2

EXPERIMENTAL DETAILS AND ANALYTICAL DATA FOR CARBONYLHYDRIDOPHOSPHINEVANADIUM COMPLEXES

Complex	Eluant	Empirical Formula (molecular mass)	Analysis (found (calcd.) (%))				
			C	H	As	P	V
HV(CO)$_4$dppm (I)	THF	$C_{29}H_{23}O_4P_2V$ (548.39)	63.1 (63.52)	4.5 (4.23)	—	11.2 (11.30)	9.0 (9.29)
HV(CO)$_4$dppe (II)	THF	$C_{30}H_{25}O_4P_2V$ (562.42)	63.6 (64.07)	4.6 (4.48)		10.8 (11.01)	8.8 (9.06)
HV(CO)$_4$dppp (III)	THF/heptane 1/1 → THF	$C_{31}H_{27}O_4P_2V$ (576.45)	63.8 (64.59)	4.9 (4.72)		10.5 (10.75)	8.9 (8.84)
HV(CO)$_4$dppb (IV)	THF/heptane 1/1	$C_{32}H_{29}O_4P_2V$ (590.48)	65.5 (65.09)	4.7 (4.95)	—	9.9 (10.49)	8.4 (8.63)
HV(CO)$_4$arphos (V)	THF	$C_{30}H_{25}AsO_4PV$ (606.37)	59.9 (59.42)	4.4 (4.16)	12.6 (12.36)	5.2 (5.11)	8.1 (8.40)
HV(CO)$_3$triphos (VI)	THF or toluene	$C_{37}H_{34}O_3P_3V$ (670.55)	66.5 (66.28)	5.3 (5.11)	—	13.5 (13.86)	7.6 (7.60)

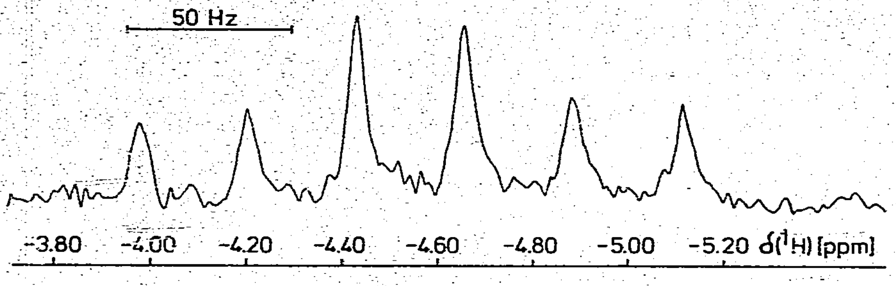

Fig. 1. The 90 MHz ^1H NMR spectrum of $HV(CO)_3\{PhP(CH_2CH_2PPh_2)_2\}$ in the hydride region at 333 K (THF solution).

They are stable for several months at 263 K under N_2. With triethylamine, hydrogen is transferred to nitrogen, and the ionic complexes $[HNEt_3][V(CO)_4\widehat{PP}]$ are recovered.

The hydride region of the ^1H NMR spectrum exhibits a simple resonance signal (symmetrical multiplet; see Table 1). Following structural assignments (pentagonal bipyramid, face-capped octahedron or trigonal prism) made for hydrido complexes of analogous composition [12], we thus assume that the hydrogen either fluctuates about the polyhedron or is fixed in a position in which the two phosphorus atoms are magnetically equivalent with respect to the H^-. For complex VI (Fig. 1), however, nuclear spin—spin interaction with the two terminal phosphorus functions is about twice that with the middle phosphorus of the ligand, indicating a distinct position of the hydrogen.

Experimental

The typical procedure below was used with appropriate adaptation for the preparation of the compounds I—VI. For experimental details and analytical data see Table 2.

300 mg $[Et_4N][V(CO)_4dppp]$ [9] dissolved in 3 ml of THF with subsequent addition of 2 ml n-heptane were passed through a silica gel column (15 × 2.5 cm; silicagel 60 puriss. 70—230 mesh ASTM, Merck.). Before use, the silica gel was dried under high vacuum for 1 h (room temperature), treated with N_2 and suspended in THF/pentane). $HV(CO)_4dppp$ was washed out, employing a total amount of about 200 ml of eluant (3 ml/min), starting with a 1/1 THF/heptane mixture, followed by mixtures successively enriched with THF, and neat THF. After evaporation to 40 ml, the solution was allowed to stand at 248 K for 1 week. Fine crystals of the complex separated out, these were filtered off and dried under high vacuum (3 h). From the filtrate, further product was isolated by treatment with heptane after concentration to 3 ml. All operations were carried out in an inert gas atmosphere.

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