

Preliminary communication

PHOSPHINE-STABILIZED DERIVATIVES OF HEXACARBONYLVANADIUM(0)

KLAUS IHMELS and DIETER REHDER

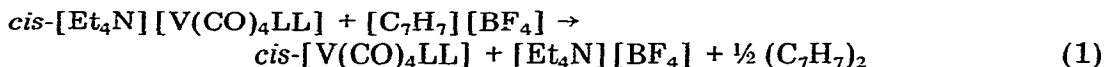
*Institut für Anorganische Chemie der Universität, Martin-Luther-King-Platz 6, D 2-Hamburg
13 (F.R.G.)*

(Received July 3rd, 1981)

Summary

The complexes *cis*-[V(CO)₄LL] (where LL is a ditertiary phosphine), V(CO)₅PPh₃ and {V(CO)₅}₂-μ-{*p*-C₆H₄(PPh₂)₂} were prepared by oxidation of the corresponding anionic compounds with tropylium tetrafluoroborate. IR and selected ESR data are presented.

Carbonyl complexes of formally zero-valent vanadium are scarce. Among the few known examples are the diamagnetic, dinuclear complexes {V(CO)₅}₂-(μ-CO)₂ [1] and [{V(CO)₄CN}]₂(μ-CN)₂] ⁴⁻ [2], and the paramagnetic species V(CO)₅PPh₃ and *cis*-[V(CO)₄dppe] [3]. We now describe a general synthesis of various derivatives of V(CO)₆ (eq. 1):



(LL = Ph₂P(CH₂)_nPPh₂, *n* = 1: dppm, *n* = 2: dppe, *n* = 3: dppp, *n* = 4: dppb; Ph₂As(CH₂)₂PPh₂: arphos; *o*-C₆H₄(PPh₂)₂: *o*-ppb). V(CO)₅PPh₃, which was characterized [3] but not isolated previously, has been prepared in this way.

The method employed is better than the decomposition of hydrido complexes [4, 5], which yields impure products, or the tedious replacement of CO ligands in V(CO)₆ by phosphines [6].

The complexes form green (dppe, arphos), olive-coloured (PPh₃) or yellow-brown (dppm, dppp, dppb, *o*-ppb) powders. They decompose rapidly on exposure to air. V(CO)₄dppm is pyrophoric. Reaction between [Et₄N]₂-[{V(CO)₅}₂-μ-(*p*-ppb)] (*p*-ppb = *p*-C₆H₄(PPh₂)₂) and [C₇H₇][BF₄] yields an olive-coloured oil of {V(CO)₅}₂-μ-(*p*-ppb). Solutions of the mono-substituted complexes in toluene decompose within several hours at room temperature. The di-substituted complexes are stable in toluene, THF and acetone; in con-

trast to the parent compound $\text{V}(\text{CO})_6$ they do not undergo disproportionation. $\text{V}(\text{CO})_4\text{dppm}$ and $\text{V}(\text{CO})_4\text{-o-ppb}$ are only slightly soluble.

The IR spectra (CO stretching region; toluene, 0.1 mm KBr cuvettes) are listed in Table 1. They show the expected pattern, i.e. four $\nu(\text{CO})$ absorptions for the di-substituted compounds of local C_{2v} symmetry, but in several cases (dppm, dppe, arphos) two bands by chance overlap. The IR spectra are very similar to those of the (diamagnetic) hydrido complexes $\text{HV}(\text{CO})_4\text{LL}$ [7] with vanadium in the formal oxidation state +1. Four bands are observed for the mono-substituted species of C_{4v} symmetry: In these complexes with bulky phosphine ligands, the Raman-active B_1 absorption (1990 cm^{-1}) becomes apparent in the IR spectrum.

TABLE 1

IR DATA

Complex	$\nu(\text{CO})\text{ (cm}^{-1}\text{)}$			
$\text{V}(\text{CO})_4\text{dppm}$	1995(sh), 1990s	1905(sh)	1875vs	
$\text{V}(\text{CO})_4\text{-o-ppb}^a$	1990s	1885(sh)	1860vs	
$\text{V}(\text{CO})_4\text{dppe}$	1995vs	1900(sh)	1858vs	
$\text{V}(\text{CO})_4\text{arphos}$	1995vs	1905(sh)	1857vs	
$\text{V}(\text{CO})_4\text{dppp}$	1993vs	1912m	1873s	1835vs
$\text{V}(\text{CO})_4\text{dppb}$	1990vs	1908m	1870s	1838vs
$\text{V}(\text{CO})_5\text{PPh}_3^b$	2050w	1990 ^c w	1920vs	1863s
$\{\text{V}(\text{CO})_5\}_2\text{-}\mu\text{-(p-ppb)}$	2040m	1990 ^c w	1910vs	1850s

^aNujol. ^bCompare ref. 3: 2052m, 1928vs (in hexane). ^c B_1 ; other: A_1 (²), E, A_1 (¹).

ESR spectra were obtained in toluene glasses ($5 \times 10^{-4}\text{ M}$, 60 K) for $\text{V}(\text{CO})_4\text{dppe}$ ($g_{\perp} = 1.9981$, $g_{\parallel} = 1.9996$) and $\text{V}(\text{CO})_4\text{dppb}$ ($g_{\perp} = 1.9989$, $g_{\parallel} = 2.0004$). The g values are smaller than those reported for $\text{V}(\text{CO})_6$ [8] ($g_{\perp} = 2.064$, $g_{\parallel} = 1.99$), which compares to a corresponding trend in ^{51}V shielding $|\delta|$ of the anionic analogues [9] ($[\text{V}(\text{CO})_6]^-$: 1952, $[\text{V}(\text{CO})_4\text{dppe}]^-$: 1796, $[\text{V}(\text{CO})_4\text{dppb}]^-$: 1724 ppm), and may well reflect the dominating influence of the strength of the ligand field on g and $|\delta|$, as predicted by theory [9]. Comparison of the g factors of carbonyl complexes with those of other vanadium(0) species [10–12] allows arrangement of the complexes in the following sequence of decreasing g ($\langle g \rangle$ or $g(\text{iso})$ in brackets): $\text{V}(\text{CO})_6$ (2.039) > $\text{V}(\text{CO})_4\text{LL}$ (1.999) > $\text{V}(\text{aryl})_2$ (1.987) > $\text{V}(\text{dipy})_3$ (1.983).

Experimental

The following procedures can be used with appropriate variation for the preparation of the $\text{V}(\text{CO})_6$ derivatives. Yields are about 55–75%. All operations must be carried out under N_2 and in dry solvents. See refs. 13 and 14 for the preparation of the anionic starting products.

$\text{V}(\text{CO})_4\text{dppe}$: A suspension of 1.07 g (1.48 mmol) of *cis*- $[\text{Et}_4\text{N}][\text{V}(\text{CO})_4\text{-dppb}]$ and 0.26 (1.48 mmol) $[\text{C}_7\text{H}_7][\text{BF}_4]$ in 50 ml toluene was stirred for 19 h at room temperature, during which it turned from red-brown to yellow-green. The solution was filtered, and the residue was washed with three 5 ml portions of toluene, and the combined filtrates were concentrated to ca. 5 ml (room

temperature, 1 Torr). Dropwise addition of 30 ml n-heptane with vigorous stirring yielded $V(CO)_4dppb$ as a yellow-brown powder. Precipitation was completed by allowing the solution to stand at 260 K for 1 day. The product was then isolated by filtration, reprecipitated from toluene/heptane, and dried under high vacuum (4 h).

$V(CO)_5PPh_3$: A suspension of 0.84 g (1.44 mmol) $[Et_4N][V(CO)_5PPh_3]$ and 0.25 g (1.44 mmol) $[C_7H_7][BF_4]$ in 40 ml toluene was cooled at 243 K and stirred for 12 h. The green solution was then filtered, combined with the washings of the residue, and evaporated to dryness (273 K, 1 Torr). The olive-coloured, powdery $V(CO)_5PPh_3$ thus obtained was washed with two 5 ml portions of pentane (200 K) and dried under high vacuum (6 h, 273 K).

References

- 1 T.A. Ford, H. Huber, W. Klotzbücher, M. Moskovits and G.A. Ozin, *Inorg. Chem.*, **15** (1976) 1666.
- 2 D. Rehder, *J. Organometal. Chem.*, **37** (1972) 303.
- 3 A. Davison and J.E. Ellis, *J. Organometal. Chem.*, **36** (1972) 131; J.E. Ellis, R.A. Faltynek, G.L. Rochfort, R.E. Stevens and G.A. Zank, *Inorg. Chem.*, **19** (1980) 1082.
- 4 J.E. Ellis and R.A. Faltynek, *J. Organometal. Chem.*, **93** (1975) 205.
- 5 U. Franke and E. Weiss, *J. Organometal. Chem.*, **152** (1978) C19.
- 6 H. Behrens, H. Brandl and K. Lutz, *Z. Naturforsch. B*, **22** (1967) 99; H. Behrens and K. Lutz, *Z. Anorg. Allgem. Chem.*, **356** (1967) 99.
- 7 U. Puttfarcken and D. Rehder, *J. Organometal. Chem.*, **185** (1980) 219.
- 8 K.A. Robinson, *J. Amer. Chem. Soc.*, **98** (1976) 5188.
- 9 D. Rehder, *Bull. Magn. Reson.*, in press.
- 10 G. Henrici-Olive and S. Olive, *J. Amer. Chem. Soc.*, **92** (1970) 4831.
- 11 C. Elschenbroich and F. Stahler, *Chimia*, **28** (1974) 730.
- 12 E. König, *Z. Naturforsch. A*, **19** (1974) 1139.
- 13 D. Rehder, L. Dahlenburg and I. Müller, *J. Organometal. Chem.*, **122** (1976) 53.
- 14 R. Talay and D. Rehder, *Chem. Ber.*, **111** (1978) 1978; *Z. Naturforsch. B*, **36** (1981) 451.