Journal of Organometallic Chemistry, 218 (1981) C54—C56
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

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), $V(CO)_5PPh_3$ and $\{V(CO)_5\}_2$-μ-$\{p$-$C_6H_4(PPh_2)_2\}$ 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 $\{V(CO)_5\}_2(\mu\text{-}CO)_2$ [1] and $[\{V(CO)_4CN\}_2(\mu\text{-}CN)_2]^{4-}$ [2], and the paramagnetic species $V(CO)_5PPh_3$ and *cis*-$[V(CO)_4$dppe$]$ [3]. We now describe a general synthesis of various derivatives of $V(CO)_6$ (eq. 1):

$$cis\text{-}[Et_4N][V(CO)_4LL] + [C_7H_7][BF_4] \rightarrow cis\text{-}[V(CO)_4LL] + [Et_4N][BF_4] + \tfrac{1}{2}(C_7H_7)_2 \quad (1)$$

(LL = $Ph_2P(CH_2)_nPPh_2$, $n = 1$: dppm, $n = 2$: dppe, $n = 3$: dppp, $n = 4$: dppb; $Ph_2As(CH_2)_2PPh_2$: arphos; o-$C_6H_4(PPh_2)_2$: *o*-ppb). $V(CO)_5PPh_3$, 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 (PPh_3) or yellow-brown (dppm, dppp, dppb, *o*-ppb) powders. They decompose rapidly on exposure to air. $V(CO)_4$dppm is pyrophoric. Reaction between $[Et_4N]_2$-$[\{V(CO)_5\}_2$-μ-(p-ppb)$]$ (p-ppb = p-$C_6H_4(PPh_2)_2$) and $[C_7H_7][BF_4]$ 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 contrast to the parent compound $V(CO)_6$ they do not undergo disproportionation. $V(CO)_4$dppm and $V(CO)_4$-*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 ν(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 $HV(CO)_4LL$ [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	ν(CO) (cm^{-1})			
$V(CO)_4$dppm	1995(sh), 1990s	1905(sh)	1875vs	
$V(CO)_4$-*o*-ppb^a	1990s	1885(sh)	1860vs	
$V(CO)_4$dppe	1995vs	1900(sh)	1858vs	
$V(CO)_4$arphos	1995vs	1905(sh)	1857vs	
$V(CO)_4$dppp	1993vs	1912m	1873s	1835vs
$V(CO)_4$dppb	1990vs	1908m	1870s	1838vs
$V(CO)_5PPh_3$^{b}	2050w	1990^{c}w	1920vs	1863s
$\{V(CO)_5\}_2$-μ-(*p*-ppb)	2040m	1990^{c}w	1910vs	1850s

^{a}Nujol. ^{b}Compare ref. 3: 2052m, 1928vs (in hexane). ^{c}B_1; other: $A_1^{(2)}$, E, $A_1^{(1)}$.

ESR spectra were obtained in toluene glasses (5×10^{-4} *M*, 60 K) for $V(CO)_4$dppe ($g_\perp$ = 1.9981, $g_\parallel$ = 1.9996) and $V(CO)_4$dppb ($g_\perp$ = 1.9989, $g_\parallel$ = 2.0004). The *g* values are smaller than those reported for $V(CO)_6$ [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] ($[V(CO)_6]^-$: 1952, $[V(CO)_4\text{dppe}]^-$: 1796, $[V(CO)_4\text{dppb}]^-$: 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*(iso) in brackets): $V(CO)_6$ (2.039) > $V(CO)_4LL$ (1.999) > $V(aryl)_2$ (1.987) > $V(dipy)_3$ (1.983).

Experimental

The following procedures can be used with appropriate variation for the preparation of the $V(CO)_6$ 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.

$V(CO)_4$dppe: A suspension of 1.07 g (1.48 mmol) of *cis*-$[Et_4N][V(CO)_4$-dppb] and 0.26 (1.48 mmol) $[C_7H_7][BF_4]$ 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 $V(CO)_4$dppb 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 vaccum (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. Rubinson, J. Amer. Chem. Soc., 98 (1976) 5188.
9 D. Rehder, Bull. Magn. Reson., in press.
10 G. Henrici-Olivé and S. Olivé, 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.