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PREPARATION AND REPLACEMENT REACTIONS OF PENTACARBONYL-(DIMETHYLSULFOXIDO)VANADATE(—I)

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Summary

The photo-reaction between $[Et_4N][V(CO)_6]$ and DMSO yields $[Et_4N]$-$[V(CO)_5DMSO]$ (with DMSO presumably bonded via sulfur). Thermally induced replacement of DMSO by a ligand L affords $[Et_4N][V(CO)_5L]$, where L = pyridine, CN^-, PCy_3, $Ph_2As(CH_2)_2PPh_2$, $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_2PEt_2$, $PhP(CH_2CH_2PPh_2)_2$ and $P(CH_2CH_2PPh_2)_3$. IR, ^{31}P and ^{51}V NMR spectra are reported.

Pentacarbonylvanadates(—I) containing phosphines, arsines and stibines have been known for several years [1], but comparatively few carbonylvanadates with the vanadium centre bonded to ligands such as SnR_3^+ and PbR_3^+ [2], NH_3 and CN^- [3], and H^- [4] have been described. There is, however, current interest in complexes with a wider range of variations in the coordination sphere. Recently, Ellis and Fjare reported on the thermal substitution of NH_3 in aminepentacarbonylvanadate by nitriles and phosphines such as $P(p\text{-}C_6H_4Cl)_3$ and $Ph_2PCH_2PPh_2$ [5]. The tedious preparation of $[V(CO)_5NH_3]^-$ in liquid ammonia [3,5,6] has prompted us to synthesize the previously unknown $[V(CO)_5$-$DMSO]^-$, which can be used alternatively, and most conveniently, as a starting material for the preparation of other pentacarbonylvanadates(—I), including those with potentially oligodentate ligands, which readily undergo photochemically induced replacement reactions with $[V(CO)_6]^-$ to give the tetra- and tricarbonylvanadates(—I) [7].

$[Et_4N][V(CO)_5DMSO]$, which is obtained in 50% yield (isolated) by UV irradiation of a THF solution containing $[Et_4N][V(CO)_6]$ and DMSO, forms an orange-coloured, air-sensitive powder. Solutions in THF are unstable unless excess DMSO is present. The replacement reactions are usually carried out in acetonitrile solution (DMSO is not replaced by CH_3CN) at room temperature by addition of excess (pyridine, $[Et_4N]CN$) or equimolar amounts of the ligand [PCy_3, $Ph_2As(CH_2)_2PPh_2$ (arphos), $Ph_2P(CH_2)_2PPh_2$ (dppe), $Ph_2P(CH_2)_2PEt_2$

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TABLE 1

SPECTROSCOPIC DATA OF THE COMPLEXES $[V(CO)_5L]^-$

L	$\nu(CO)$ [a] (cm^{-1})					$\delta(^{51}V)$ [b] (ppm)		$\delta(^{31}P)$ [c] (ppm)	
DMSO [d]	1975w		1850sh	1830vs		−1657		—	
pyr	1960w		1860s	1825vs	1805vs	−1463		—	
CN^-	1950w		1860m	1800vs	1750s	−1864		—	
PCy_3	1955m		1855m	1815vs		−1875			
arphos	1965m		1860m	1820vs		−1825 [e]	−1847 (270)	−12.4	
dppe	1955m	1885sh	1850m	1815vs		−1843 (280)		−12.9	
pepe	1960m	1890w	1850s	1810vs		−1847 (270)	−1890 [f] (215)	−14.5	PEt_2: −21.3 [g]
p_3	1953m	1885w	1860s	1810vs		−1846		−13.3	PPh: −16.9
pp_3	1960m	1875w	1860m	1810vs		−1846		−13.3	P: −18.3

[a] In toluene. [b] Relative $VOCl_3$; in brackets: ^{51}V—^{31}P coupling (not resolved if not indicated). [c] Data (at 305 K) are given for the uncoordinated PPh_2-functions. The resonances are complex, showing that isomeric mixtures of conformers are present; the centres only are indicated. The ^{31}P resonances for ligated P are usually broadened (by interaction with the 7/2 nucleus ^{51}V) to an extent, where valid information is no longer accessible. [d] DMSO region (Nujol mull): $\nu(SO)$ 1050m, $\delta(CH_3)$ 1005m; other: 705w, 675w, 650s, 638s, 460m cm^{-1}. [e] V—$AsPh_2$, weak signal (see also Ref. 13). [f] V—PEt_2. [g] An additional broad signal at +49 ppm (250 K) corresponds with PEt_2 coordinated to vanadium.

(pepe), $PhP(CH_2CH_2PPh_2)_2$ (p_3), $P(CH_2CH_2PPh_2)_3$ (pp_3)], and are terminated after ca. 1/2 h of stirring. Oligodentate ligands tend to form chelate structures by replacing additional CO groups if the solutions are exposed to diffuse daylight and allowed to stand for several days.

Spectroscopic data are listed in Table 1. The CO stretching region of the IR spectra shows four absorptions, which, following recent work by Darensbourg and Hanckel [8], may be assigned in the following way: The sharp band of weak to medium intensity at ca. 1955 is the $A_1^{(2)}$ mode, the weak shoulder at ca. 1885 cm^{-1} B_1. $A_1^{(1)}$ and E accidentally overlap (ca. 1810 cm^{-1}), and the absorption around 1855 cm^{-1} might be due to impurities of $[V(CO)_6]^{-1}$. It should be noted, however, that $[V(CO)_6]^-$ was detected in the ^{51}V NMR spectrum to a negligible amount only (very sharp signal at —1952 ppm).

The question arises of DMSO is bonded via the sulfur or the oxygen function. The two IR bands which are generally used in this context are $\nu(SO)$ and $\delta(CH_3)$. The latter is close to 1000 [9], hence the absorption at 1005 cm^{-1} in our complex (Nujol mull) can be assigned the methyl group. Then, the band at 1050 cm^{-1} is the SO stretching mode of coordinated DMSO. This mode is reported to shift to higher wave numbers $\tilde{\nu}$ relative to free DMSO [$\nu(SO)$ 1055 cm^{-1}], if the ligand is coordinated via sulfur, and to lower $\tilde{\nu}$, if coordination occurs through oxygen [10]. Although there is a slight shift to lower $\tilde{\nu}$, O-coordination is unlikely to occur in $[V(CO)_5DMSO]^-$; the relatively low $\nu(SO)$ of the S-bonded DMSO may be induced by the low-valent metal centre.

S-coordination is further supported by consideration of the ^{51}V chemical shift $\delta(^{51}V)$. Herberhold has shown that in $CpV(NO)_2L$ complexes (where L is, inter alia, a N or O ligand), the lowest shielding of the ^{51}V nucleus is associated with oxygen ligands [11]. Furthermore, S-bonded DMSO in carbonylrhodium complexes imparts a higher ^{103}Rh shielding than O-bonded DMSO [12]. The $\delta(^{51}V)$ of $[V(CO)_5DMSO]^-$, exceeding that of $[V(CO)_5pyr]^-$ by almost 200 ppm, favours S-coordination.

$\delta(^{51}V)$ values are also of interest in the light of competing replacement reactions with oligodentate ligands carrying different donor/acceptor functions: While arphos, p_3 and pp_3 are ligated almost exclusively via the diphenylphosphino group [$\delta(^{51}V)$ —1845 ± 2 ppm], pepe coordinates equally through PPh_2 and PEt_2.

Experimental

All operations were carried out under nitrogen and in dry, oxygen-free solvents.

$[Et_4N][V(CO)_5DMSO]$

2.3 g $[Et_4N][V(CO)_6]$ (6.6 mmol), dissolved in ca. 100 ml THF, were treated with 2.5 ml DMSO (ca. 40 mmol) and irradiated for 6 h. The UV source (a high pressure mercury lamp in a cooled quartz immersion well) was placed close to the Duran reaction vessel. During the irradiation, a weak N_2 stream was bubbled through the solution. The mixture was subsequently concentrated to 10 ml, and 100 ml of n-heptane were immediately added. After stirring for a few minutes, a red oil (the complex dissolved in DMSO) separated out. The colourless, super-