

Alkyl and Aryl Migration in Biscyclopentadienyl-alkyl- or -phenyl-vanadium(III)

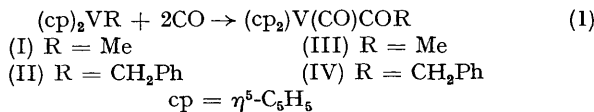
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Summary Reaction of carbon monoxide with biscyclopentadienyl-methyl- or -benzyl-vanadium(III) gave carbonylbiscyclopentadienylacylvanadium(III), while under the same conditions biscyclopentadienylphenylvanadium(III) yielded dicarbonyl (phenyl- η^4 -cyclopentadiene)(η^5 -cyclopentadienyl)vanadium(I) which forms carbonyl-(cyclopentadienyl)(phenylcyclopentadienyl)vanadium(II) via phenyl migration to a cyclopentadienyl ligand.

ALKYL or aryl labilisation by nucleophilic attack seems to be a general characteristic of σ -organometallic derivatives of transition metals. This labilisation can be interpreted as a consequence of orbital occupation of the metal by the nucleophile followed by migration of the labilised alkyl or aryl group on to the entering nucleophile or on to another ligand already co-ordinated to the metal.¹ Reactions of biscyclopentadienyl-alkyl or -phenyl complexes of vanadium(III) with carbon monoxide are good illustrations of the general pattern of reactivity of carbon-metal σ -bonds.¹

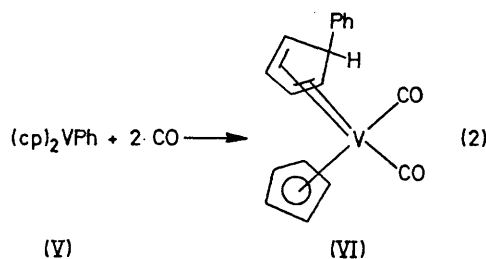
When methylbiscyclopentadienylvanadium(III) (I), or benzylbiscyclopentadienylvanadium(III) (II),² were treated at room temperature, in toluene or heptane solution, with CO at atmospheric pressure, 2 mol of CO per vanadium were absorbed to give complexes (III)† and (IV)† (ca. 60%) [reaction (1)], which were obtained as green-maroon



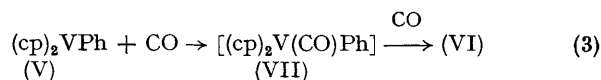
crystals by cooling the solution to -80°C . The complexes (III) and (IV) are soluble in aromatic hydrocarbons and monomeric in benzene [(III): M 263; $\nu(\text{THF})$ 1904 (CO) and 1605 (acyl CO); τ (C_6D_6) 5.63 (10H, s) and 7.44 (3H, s); (IV): M 338; $\nu(\text{THF})$ 1903 (CO) and 1615 (acyl CO); τ (C_6D_6) 2.80 (5H, m), 5.67 (10H, s), and 5.86 (2H, s)].

Compound (V)³ absorbed two moles of CO per vanadium (in toluene at 16°C), giving a red crystalline, thermally unstable compound (VI). Its i.r. and n.m.r. spectra [two CO stretching bands of similar intensity at 1861 and 1929 cm^{-1} (THF) with a medium intensity C-H stretch at 2750 cm^{-1} (Nujol); τ (C_6D_6) 6.47 (2H, m), 5.80 (5H, s), 5.24

(2H, m), 4.90 (1H, m), and 2.65 (5H, m)], satisfactory analytical results and its diamagnetism lead us to formulate complex (VI) as $(\eta^5\text{-C}_5\text{H}_5)(\eta^4\text{-C}_5\text{H}_5\text{Ph})\text{V}(\text{CO})_2$. The similar, diolefinic π -cyclopentadienylvanadium(I) can be obtained from $\text{V}(\text{cp})(\text{CO})_4$ by reaction with a diolefin.⁴

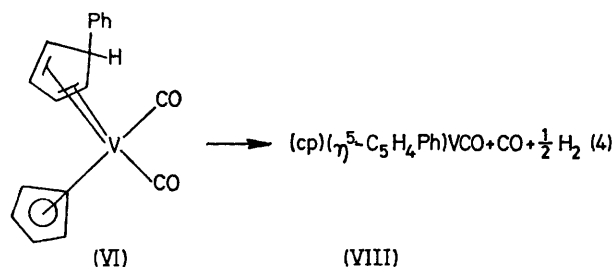


Complex (VI) [reaction (2)] can be interpreted as arising from direct nucleophilic attack of the phenyl residue on the cyclopentadienyl ligand induced by the incoming CO. This assumption is supported by the i.r. spectrum of toluene or THF solutions measured during the CO adsorption which show three bands [1861, 1905, and 1929 cm^{-1}] in the carbonyl region and no band in the acyl region, with the 1905 cm^{-1} band disappearing at the end of the carbonylation. The 1905 cm^{-1} band can reasonably be attributed to the phenyl carbonyl species (VII), a precursor to (VI).



The formation of (VI) via an acyl intermediate similar to (III) and (IV) seems to be excluded by the absence of an acyl band in conjunction with the 1905 cm^{-1} band, during the carbonylation of (V).

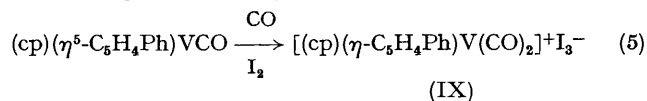
Carbon monoxide is evolved rapidly from compound (VI), both in the solid state and in toluene solution at $25\text{--}30^\circ\text{C}$, following the stoichiometry in reaction (4) and giving the monocarbonyl (VIII), m.p. 46°C . This formulation as a seventeen-electron carbonyl vanadium is consistent with its analytical results, monomeric nature in benzene (M 278), $\nu(\text{CO})$ (heptane) 1893 cm^{-1} , and magnetic moment (1.87 B.M. at 291). A carbonylvanadium analogues



to (VIII) can be obtained by carbonylation of $V(cp)_2$ [$\nu(CO)$ 1881 cm^{-1}].⁵

Further evidence supporting the formulation (VIII) is its conversion into the corresponding ionic dicarbonyl of vanadium(III) obtained by oxidation with I_2 under CO.

The diamagnetism of (IX) was shown by its n.m.r. spectrum:



$\tau[(CD_3)_2CO]$ 4.15 (5H, s), 3.93 (2H, m), 3.36 (2H, m), and 2.43 (5H, m), and it had analytical results and an i.r. spectrum [$\nu(CO)$ (Nujol) 2000, 2040 cm^{-1}] consistent with this formulation. A similar oxidation⁸ of $V(cp)_2CO$ with I_2 under CO gave the known $[V(cp)_2(CO)_2]^+ I_3^-$.⁶

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⁶ F. Calderazzo and S. Bacciarelli, *Inorg. Chem.*, 1963, **2**, 721.

† Satisfactory elemental analytical data were obtained.