Journal of Organometallic Chemistry, 367 (1989) C18–C20
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 9918PC

Preliminary communication

Facile synthesis and reactivity of CO-free monocyclopentadienylvanadium(I) alkyne complexes

Bart Hessen and Jan H. Teuben *

Department of Chemistry, Rijksuniversiteit Groningen, Nijenborgh 16, 9747 AG Groningen (The Netherlands)

(Received January 16th, 1989)

Abstract

Reactive CO-free monocyclopentadienylvanadium(I) complexes $CpV(\eta^2\text{-}RC{\equiv}CR')(PMe_3)_2$ (R,R′ = Ph,Ph; Ph,Me; Et,Et) can be synthesized by Mg reduction of $CpVCl_2(PMe_3)_2$ in the presence of free alkyne. Reaction with a second alkyne, or use of diynes in the reduction, produces metallacycles with the metallacyclopentatriene structure.

The chemistry of CpV^I complexes has been much studied since the discovery of $CpV(CO)_4$ [1], but with very few exceptions [2,3] all the compounds obtained still contain strongly bound CO ligands, which considerably restrict the range of reactions [4*]. Recently we reported $CpV(\eta^2\text{-ethylene})(PMe_3)_2$, in which the labile ethylene ligand can be easily replaced by other ligands such as diphenylacetylene or 2,2′-bipyridine [5]. The complexes $CpV(\eta^2\text{-}RC{\equiv}CR')(PMe_3)_2$ (R,R′ = Ph,Ph (**1**); Ph,Me (**2**); Et,Et (**3**)) can be very conveniently synthesized (in 60–85% yield) by magnesium reduction of $CpVCl_2(PMe_3)_2$ [6] in THF in the presence of free alkyne [7*].

$$CpVCl_2(PMe_3)_2 + Mg + RC{\equiv}CR' \rightarrow CpV(RC{\equiv}CR')(PMe_3)_2$$

(**1**: R,R′ = Ph,Ph;
2: R,R′ = Ph,Me;
3: R,R′ = Et,Et)

This procedure is not limited to alkyne complexes, but can also be used to prepare other hydrocarbon derivatives, such as the diene complex $CpV(\eta^4\text{-2,3-dimethyl-1,3-butadiene})PMe_3$.

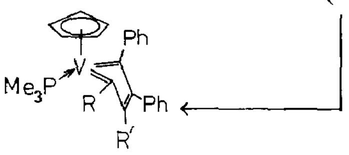
Compounds **1**–**3** are diamagnetic, the ^{13}C NMR resonances of the acetylenic carbons (**1**: 226.8 ppm; **3**: 225.6 ppm) indicate that the alkyne acts as a 4-electron

---

* Reference numbers with asterisks indicate notes in the list of references.

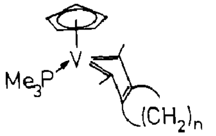
donor as in CpV(RC≡CR′)(CO)L (L = CO, PR_3) [8]. Complex **2** reacts at room temperature with 2-butyne initially to form the labile (but isolable) intermediate CpV(η^2-PhC≡CPh)(η^2-MeC≡CMe)PMe_3 (**4**), and this is followed by coupling of the alkynes to yield the metallacycle CpV($C_4Me_2Ph_2$)PMe_3 (**5**).

$$\underset{(1)}{CpV(PhC{\equiv}CPh)(PMe_3)_2} + MeC{\equiv}CMe \rightarrow \underset{(4)}{CpV(PhC{\equiv}CPh)(MeC{\equiv}CMe)PMe_3}$$



(5)

NMR data indicate that **5** has the bent metallacyclopentatriene structure, as recently found for CpMo(C_4Ph_4)Cl by Hirpo and Curtis [9], and as predicted by MO considerations for complexes of this type with a formal d^2-configuration [10]. The compound is diamagnetic, with the ^{13}C NMR resonances of the metallacycle strongly shifted downfield (δ 273 and 257 ppm) for the two vanadium bound carbon atoms, and upfield (δ 80.80 and 88.71 ppm) for the other two. Metallacycles **6** and **7** are formed directly when $CpVCl_2(PMe_3)_2$ is reduced in the presence of 2,7-nonadiyne or 2,8-decadiyne respectively.



(6 : n = 3 ;
7 : n = 4)

Preliminary studies show that the CO-free alkyne complexes are much more reactive than their CO-containing counterparts, and react readily with substrates such as ethylene and butadiene to form C,C coupling products. Full details of the reactions will be given elsewhere.

Acknowledgement. This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO). We thank Dorinda Veenstra for experimental assistance.

References

1 E.O. Fischer and W. Haffner, Z. Naturforsch. B, 9 (1954) 503.
2 R.B. King and K.-N. Chen, Inorg. Chim. Acta, 23 (1977) L19.
3 (a) A.W. Duff, K. Jonas, R. Goddard, H.-J. Kraus and C. Krüger, J. Am. Chem. Soc., 105 (1983) 5479. (b) K. Jonas, W. Rüsseler, K. Angermund and C. Krüger, Angew. Chem., 98 (1986) 904.
4 For reactivity of CpV(RC≡CR)$(CO)_2$ see: (a) A. Nesmeyanov, K.N. Anisimov, N.E. Kolobova and A.A. Pasynskii, Dokl. Akad. Nauk. SSSR, 182 (1968) 112; (b) 185 (1969) 610; (c) D.F. Foust and M.D. Rausch, J. Organomet. Chem., 239 (1982) 321.
5 B. Hessen, A. Meetsma and J.H. Teuben, J. Am. Chem. Soc., 110 (1988) 4860.
6 J. Nieman, J.H. Teuben, J.C. Huffman and K.G. Caulton, J. Organomet. Chem., 155 (1983) 193.

7 Preparation of complex **1**: a mixture of $CpVCl_2(PMe_3)_2$ (1.784 g, 5.26 mmol), diphenylacetylene (0.938 g, 5.26 mmol) and magnesium turnings (1.0 g, excess) in 30 ml of THF was stirred under nitrogen at room temperature for 5 h. The solvent was removed in vacuo and the mixture extracted with toluene. Concentration of the extract, addition of some pentane, and cooling to −80 °C yielded 2.005 g (4.49 mmol, 85%) of deep red crystalline **1**. Found: C, 67.20; H, 7.46; V, 11.43. $C_{25}H_{33}VP_2$ calcd: C, 67.26; H, 7.45; V, 11.41%.

8 H.G. Alt and H. Engelhardt, Z. Naturforsch. B, 40 (1985) 1134.

9 W. Hirpo and M.D. Curtis, J. Am. Chem. Soc., 110 (1988) 5218.

10 M.D. Curtis and J. Real, J. Am. Chem. Soc., 108 (1986) 4668.