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Preliminary communication

DICARBONYL(METHYLCYCLOPENTADIENYL)MANGANESE COMPLEXES OF 4-VINYLPYRIDINE

JOHN M. KELLY and CONOR LONG
Department of Chemistry, Trinity College, Dublin 2 (Ireland)

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Summary

The synthesis and characterisation by their IR and NMR spectra of both *N*-bound and π-bound (MeCp)$(CO)_2$Mn(VP) and of the bridged complex (MeCp)$(CO)_2$Mn(μ-VP)Mn$(CO)_2$(MeCp) are reported.

It is well known that (MeCp)$(CO)_2$Mn and Cp$(CO)_2$Mn (Cp = η^5-C_5H_5: MeCp = η^5-MeC_5H_4) may bond to *n*-donor or π-donor ligands, although there are very few reported examples of complexes where a ligand containing both functionalities acts separately as a monodentate *n*-donor, monodentate π-donor or as a bridging *n*- and π-donor [1,2]. We report here three compounds of 4-vinylpyridine (VP) in which this behaviour is observed. In known examples of 4-vinylpyridine-metal complexes, the ligand is bound to the metal centre via the pyridine nitrogen atom and to the best of our knowledge there are no previous reports of coordination through the vinyl group [3—7].

The products were formed on addition of an ethanol solution of (MeCp)-$(CO)_2$Mn(EtOH) (prepared in situ by photolysis of (MeCp)$(CO)_3$Mn in ethanol) to vinylpyridine and subsequent removal of the solvent (see Scheme 1). When a two-fold molar excess of 4-vinylpyridine is used, I and II are produced in good yield in ratio 4/1, whereas III is the major product with half-equivalent amounts of 4-vinylpyridine. The products are readily separated by chromatography on neutral alumina, eluting with benzene. I and III elute readily from the column, whereas II elutes much more slowly, presumably because of interaction of the free pyridine function with the alumina.

IR (ν(CO)) and NMR data for the complexes are given in the Tables 1 and 2. I and III show ν(CO) bands in positions close to those recorded for other Cp$(CO)_2$Mn complexes of substituted pyridines [2,8] while in II and III ν(CO) bands characteristic of Cp$(CO)_2$Mn (olefin) complexes [8,9] are found. In the ^{1}H NMR, complex I shows signals characteristic of uncoordinated vinyl groups

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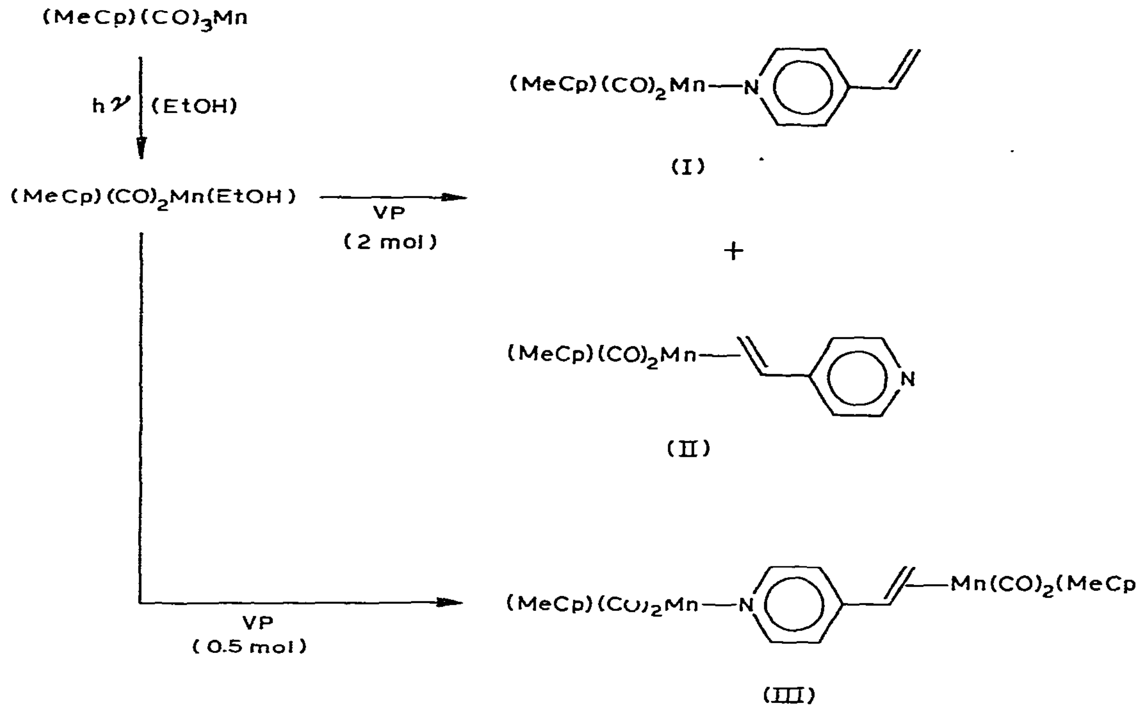

SCHEME 1

TABLE 1

INFRARED (CARBONYL STRETCH) ABSORPTIONS FOR I, II AND III

Compound	Solvent	ν(CO) (cm^{-1})
I	Isooctane	1928, 1863
II	Isooctane	1974 (br)^a, 1916
III	Isooctane	1975, 1922 (br), 1859

[a] On purification on an alumina column this peak appears to be split into two components at 1976 and 1971 cm^{-1}. The origin of this effect is uncertain.

TABLE 2

^{1}H NMR DATA (80 MHz; C_6D_6)

Compound	Pyridine ring protons	Vinyl protons	Cp-ring protons	Methyl protons
I	8.2 —8.4 (2H,m) 5.95—6.15 (2H,m)	5.7—6.25 (1H,m) 5.1—5.5 (1H,m) 4.8—5.05 (1H,m)	4.1—4.3 (2H,m) 3.9—4.1 (2H,m)	1.27 (3H,s)
II	8.1 —8.5 (2H,m) 5.8 —6.1 (2H,m)	3.1—3.5 (1H,m) 2.0—2.5 (2H,m)	3.5—3.7 (4H,m)	1.37 (3H,s)
III	8.2 —8.4 (2H,m) 5.8 —6.0 (2H,m)	3.0—3.3 (1H,m) 2.1—2.5 (2H,m)	4.2—4.4 (2H,m) 3.9—4.1 (2H,m) 3.5—3.8 (4H,m)	1.36 (3H,s) 1.33 (3H,s)

as found in the free ligand or in complexes such as [Ru^{II}(bpy)$_2$(VP)X]$^{n+}$ [5] or M(CO)$_5$(VP) (M = Cr, Mo or W) [6] where the ligand is bound to the metal. In II and III however the vinyl protons are strongly shifted to higher field as is expected for coordinated olefins [9]. (Figure 1 gives spectrum of III).

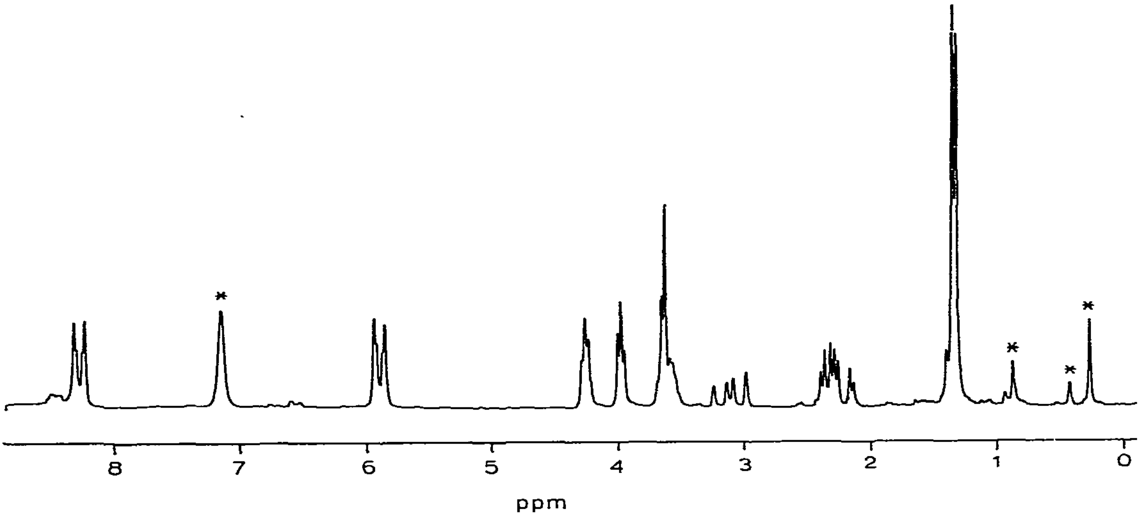

Fig. 1. 80 MHz ^{1}H NMR of $(MeCp)(CO)_2Mn(\mu\text{-VP})Mn(CO)_2(MeCp)$ (III) in C_6D_6 solution (* solvent and solvent impurities).

The *N*-bound complexes are appreciably more oxygen sensitive than their π-bound counterparts. Indeed in solution III is converted to II by addition of oxygen, the reaction being conveniently monitored by IR. Photolysis of the bridged complex III with visible light yields II and $(MeCp)(CO)_3Mn$ as products. The selective cleavage of the M—N bond observed here is possible because of the strong absorption in the visible of the *N*-bound complex (λ_{max} is at 425 nm for I in ethanol, λ_{max} for III at 438 nm in toluene, whereas the π-bound complex absorbs only very weakly in this region of the spectrum (λ_{max} at 307 nm for II in ethanol)).

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References

1 K.G. Caulton, Coord. Chem. Rev., 38 (1981) 1.
2 W. Strohmeier, Angew. Chem. Int. Ed. Engl., 3 (1964) 730.
3 S. Tazuke and S. Okamura, J. Polymer Sci., Part A-1, 5 (1967) 1083.
4 N.H. Agnew, R.J. Collin and L.F. Larkworthy, J. Chem. Soc., Dalton Trans., (1974) 272.
5 J.M. Clear, J.M. Kelly, C.M. O'Connell, and J.G. Vos, J. Chem. Res. (S), (1981) 260; J. Chem. Res. (M), (1981) 3039.
6 J.M. Kelly and C. Long, manuscript in preparation.
7 M. Kaneko and E. Tsuchida, Macromol. Rev., 16 (1981) 397.
8 P.J. Giordano and M.S. Wrighton, Inorg. Chem., 16 (1977) 160.
9 R.J. Angelici and W. Loewen, Inorg. Chem., 6 (1967) 682.