

4-Vinylpyridine complexes of group VIB metals: Syntheses, reactions and spectral features

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Received 31 January 1989; accepted 10 April 1989

Reactions of $[M(CO)_6]$ or $[M(CO)_3(MeCN)_3]$ ($M = Cr, Mo$ or W) with 4-vinylpyridine lead to the complexes having the formulation $[(4-CH_2=CH-C_5H_4N)M(CO)_3]$ (I) in which 4-vinylpyridine is bonded to the metal atom through the six π -electrons of the heteroaromatic ring. Reaction of I ($M = Cr$) with HCl gas affords the N-protonated complex $[4-CH_2=CH-C_5H_4NH)Cr(CO)_3]Cl$ (II). Complexes (I) ($M = Cr$ or Mo) also react with PPh_3 to give $[M(CO)_3(PPh_3)_3]$ (III).

The synthesis of arene substituted derivatives of Group VIB metal carbonyls and their applications as reagents for organic synthesis or as precursors for new organometallic complexes have been known¹ for a long time. Although aromatic heterocycles such as thiophene and pyrrole have been reported^{2,3} to coordinate to $M(CO)_3$ groups, complexes of pyridine or substituted pyridine systems have remained mostly unexplored. We report herein the syntheses, reactions and spectral characteristics of some 4-vinylpyridine substituted derivatives of Group VIB metal carbonyls.

Materials and Methods

Reactions were carried out under a dry nitrogen atmosphere or *in vacuo*. IR spectra were recorded on a PE 983 spectrophotometer, PMR spectra in $CDCl_3$ or CD_2Cl_2 on a Varian XL-200 instrument and mass spectra on a high resolution mass spectrometer. Acetonitrile was freshly distilled over P_2O_5 . $[M(CO)_6]$ ($M = Cr, Mo$ or W) was commercially available. $[M(CO)_3(MeCN)_3]$ was prepared following published procedures⁴⁻⁶.

Preparation of complexes (I)

These were prepared by two methods (A) and (B).

Method A: A mixture containing $[Cr(CO)_6]$ (1 g, 4.5 mmole), 4-vinylpyridine (1.44 g, 13.7 mmole) and heptane (50 ml) was degassed, sealed *in vacuo* and heated at 100-120° for 72 hr. The reaction mixture was cooled and the orange solution filtered through kiesel-guhr. After removal of solvent under reduced pressure the residue was chromatographed over a column of silica gel. Elution with pet. ether (40-60°)-diethyl ether (1:1, v/v) gave two bands.

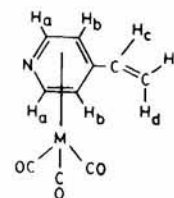
The first band upon removal of solvent under reduced pressure gave $[(4-CH_2=CH-C_5H_4N)-Cr(CO)_3]$ as yellow crystals from pentane-diethyl ether (0.6 g, 55%), m.p. 118-20° (Found: C, 50.4; H, 3.2; N, 5.9. $C_{10}H_7NO_3Cr$ requires C, 49.8; H, 3.0; N, 5.8%). The second band upon removal of solvent gave a small quantity of an uncharacterised material.

Complexes I ($M = Mo$), m.p. 109-11°, yield 60% (Found: C, 42.7; H, 2.8; N, 4.5. $C_{10}H_7NO_3Mo$ requires C, 42.1; H, 2.5; N, 4.9%) and I ($M = W$), m.p. 136-38°, yield 40% (Found: C, 32.7; H, 2.4; N, 4.1. $C_{10}H_7NO_3W$ requires C, 32.2; H, 1.9; N, 3.8%) were similarly prepared.

Method B: To a freshly prepared solution of $[Cr(CO)_3(MeCN)_3]$ (1.18 g, 4.6 mmole) in acetonitrile (50 ml) was added 4-vinylpyridine (1.44 g, 13.7 mmole) and the reaction mixture refluxed for 2 hr. Work-up as described under (A) gave I ($M = Cr$) (0.79 g, 72%). Complexes I ($M = Mo$ and W) were obtained in 68% and 56% yields respectively by this method.

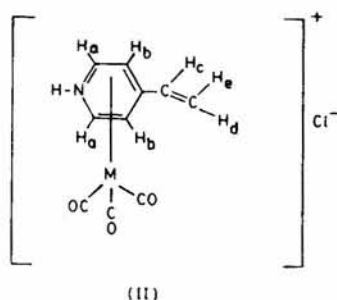
Reaction of I ($M = Cr$) with hydrogen chloride

Hydrogen chloride was bubbled through a solution of I ($M = Cr$) (0.5 g, 2.07 mmole) in hexane (50 ml). A pale yellow precipitate immediately separated out. After 4 hr, the precipitate was filtered,



(I)

washed with pentane and dried *in vacuo* to afford [(4-CH₂=CHC₅H₄NH)(Cr(CO)₃)Cl (II) (0.92 g, 80%) as pale yellow crystals, m.p. 165-67° (Found: C, 44.5; H, 3.1; N, 5.2; C₁₀H₈NO₃ClCr requires C, 44.2; H, 2.8; N, 5.3%).



Reaction of I (M = Cr) with triphenylphosphine

A solution of I (M = Cr) (0.5 g, 2.07 mmole) and triphenylphosphine (1.58 g, 6.21 mmole) in cyclohexane (50 ml) was heated to reflux under nitrogen for 4 hr. The colour of the solution turned pale yellow. The solvent was removed under reduced pressure and the solid thus obtained was washed several times with pentane to yield [Cr(CO)₃(PPh₃)₃] (ref. 7) (0.65 g, 66%), as pale yellow crystals. I (M = Mo) reacted with PPh₃ in a similar way to give [Mo(CO)₃(PPh₃)₃] (ref. 8) (72%).

Results and Discussion

[M(CO)₆] or [M(CO)₃(MeCN)₃] (M = Cr, Mo or W) react with 4-vinylpyridine to give the new complexes of the composition [(4-CH₂=CH-C₅H₄N)M(CO)₃] (I) by the loss of three CO groups or the acetonitrile ligands. Elemental analyses were compatible with the assigned formulation I.

The IR spectra of I in cyclohexane exhibited two νCO modes in each of the complexes [(M = Cr), 1936 and 1916 cm⁻¹; (M = Mo), 1940 and 1919 cm⁻¹ and (M = W), 1930 and 1916 cm⁻¹] in agreement with the C_{3v} symmetry. Similar νCO modes have been reported in the literature⁹⁻¹¹ for the arene and substituted arene-tricarbonyl complexes of Gr VIB metals.

PMR spectra indicated the presence of the 4-vinylpyridine ligand bonded to the metal through the heteroaromatic ring. Thus the PMR spectra [I (M = Cr), CDCl₃, δ 8.38 (d, J = 6.6 Hz, 2H), 7.07 (d, J = 6.6 Hz, 2H), 6.62 (dd, J = 17.3 and 10.8 Hz, 1H), 6.01 (d, J = 17.3 Hz, 1H), 5.63 (d, J = 10.8 Hz, 1H); I (M = Mo), CD₂Cl₂, δ 8.56 (d, J = 6.6 Hz, 2H), 7.22 (d, J = 6.6 Hz, 2H), 6.64 (dd, J = 17.6 and 10.8 Hz, 1H), 6.02 (d, J = 17.6 Hz, 1H), 5.64 (d, J = 10.8 Hz, 1H); I (M = W), CDCl₃, δ 8.25 (d, J = 5.9 Hz,

2H), 7.55 (d, J = 5.9 Hz, 2H), 6.80 (dd, J = 17.5 and 11.5 Hz, 1H), 6.05 (d, J = 17.5 Hz, 1H), 5.60 (d, J = 11.5 Hz, 1H)] comprised of two doublets for the *para* substituted pyridine ring, a double doublet for H_c and doublets for both H_d and H_e. The double doublet for H_c arises due to coupling of the non-equivalent H_d and H_e. The doublets at ~δ 6.0 and 5.6 are due to H_d and H_e respectively. The assignment is made on the basis of the large *trans* coupling constant [³J(HCCH) ~ 17 Hz] between the H_d and H_e protons. The observed values of *cis* and *trans* coupling constants are compatible with those observed for a vinylic system¹². The chemical shifts for the vinylic protons remain almost unchanged while those of the pyridine ring protons are slightly shifted towards higher field indicating that complexation occurs through the six π-electrons of pyridine ring. The assigned structure is also consistent with the 18-electron rule formalism. The mass spectra of complexes (I) displayed the molecular ion peaks corresponding to the formulation [(CH₂=CH-C₅H₄N)M(CO)₃]. Other important peaks due to the sequential loss of three CO groups were also observed [I (M = Cr), m/z at 241 (M⁺), 213 (M⁺-CO), 185 (M⁺-2CO), 157 (M⁺-3CO), 105 {M⁺-(3CO + Cr)}; I (M = Mo), m/z at 285 (M⁺), 257 (M⁺-CO), 229 (M⁺-2CO), 201 (M⁺-3CO), 105 {M⁺-(3CO + Mo)}; I (M = W), m/z at 373 (M⁺), 345 (M⁺-CO), 317 (M⁺-2CO), 289 (M⁺-3CO), 105 {M⁺-(3CO + W)}]. These fragmentation patterns are characteristic of metal carbonyl complexes¹³.

The complex I (M = Cr) reacts with HCl gas at ambient temperature to give the N-protonated product [(4-CH₂=CH-C₅H₄NH)Cr(CO)₃Cl (II) as pale yellow crystals. IR spectrum of II in CH₂Cl₂ exhibited two νCO bands at 2035 and 1990 cm⁻¹. The shift of the νCO modes from 1936 and 1916 cm⁻¹ in I (M = Cr) to 2035 and 1990 cm⁻¹ in II is consistent with the removal of electron density from the chromium atom as expected for a cationic complex. Complex (II) also displayed a broad band at 3170 cm⁻¹ characteristic of νNH supporting the formation of the N-protonated complex. The PMR spectrum of II [CD₂Cl₂, δ 8.71 (d, J = 6.6 Hz, 2H), 7.57 (d, J = 6.6 Hz, 2H), 6.92 (dd, J = 17.5 and 10.7 Hz, 1H), 6.38 (d, J = 17.5 Hz, 1H), 5.94 (d, J = 10.7 Hz, 1H)] is also consistent with the proposed structure except that we failed to observe the signal due to NH proton. The mass spectrum of II [m/z 278 (M⁺), 250 (M⁺-CO), 222 (M⁺-2CO), 194 (M⁺-3CO), 106 {M⁺-(3CO + Cr + Cl)} 105 {M⁺-(3CO + Cr + HCl)}] showed the molecular ion peak at m/z 278 corresponding to the molecular formula [(CH₂=CHC₅H₄NH)Cr(CO)₃]Cl. Other important peaks due to successive loss of three carbonyl

groups were also observed in the spectrum. The peak at m/z 106 corresponding to $\text{CH}_2 = \text{CHC}_5\text{H}_4\text{NH}$ clearly indicated the formation of N-protonated complex.

Reaction between **I** ($M = \text{Cr}$ or Mo) and triphenylphosphine in cyclohexane occurred at reflux temperature to give complexes $[\text{M}(\text{CO})_3(\text{PPh}_3)_3]$ (**III**) which were characterised from a comparison of their spectral data with those of authentic samples reported in the literature^{7,8}. The formation of **III** from **I** provides further evidence that in complexes (**I**) the organic ligand is bonded to the $\text{M}(\text{CO})_3$ moiety. This reaction seems to be analogous to the reaction of PPh_3 with arenetricarbonyl complexes of Group VIB metals¹⁴.

Acknowledgement

The PMR and mass spectra were procured by the courtesy of the Department of Chemistry, University College London and the Research School of Chemistry, Australian National University, Australia.

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