The First Transition Metal Complex Containing a Co-ordinated Vinylcyclopropene and its Photochemical Ring Expansion to give an η^4 -Cyclobutadiene Ligand

Richard C. Hemond and Russell P. Hughes*

Chemistry Department, Dartmouth College, Hanover, NH 03755, U.S.A.

1,2,3-Triphenyl-3-trifluorovinylcycloprop-1-ene (**1a**) reacts with $[Fe_2(CO)_9]$ to give the first example of a complex (**3**) containing a co-ordinated η^2 -vinylcyclopropene; on subsequent irradiation an unprecedented ring expansion reaction occurs to give the η^4 -cyclobutadiene complex (**4**).

The thermal and photochemical ring expansion reactions of vinylcyclopropenes to afford substituted cyclopentadienes and indenes have been a topic of considerable interest.¹ Recent studies have focused on the thermal, transition metal promoted chemistry of vinylcyclopropenes.^{2—5} We have previously described the synthesis of 1-metallacyclohexa-2,4-diene complexes in which the initial co-ordination of the vinyl-cyclopropene to the metal centre appears to be followed by



(5)

oxidative cleavage of a cyclopropene C–C bond.^{2,3} Others have recently described catalytic transformations of vinylcyclopropenes to give substituted phenols *via* incorporation of CO.^{4,5} Studies in which transition metal binding can be unambiguously shown to affect the photochemistry of coordinated ligands are less well known. We now report isolation of the first example of a transition metal complex containing an unopened, co-ordinated vinylcyclopropene ligand, and its subsequent photochemical transformation to a co-ordinated cyclobutadiene ring *via* a formal [1,2] fluorine shift and a concomitant expansion from a three- to a four-membered ring.

Treatment of triphenylcyclopropenyl hexafluorophosphate⁶ with the alkenyl cadmium reagent $[CdI(CF=CF_2)]^7$ in rigorously dry dimethylformamide (DMF) affords 1,2,3-triphenyl-3-(trifluorovinyl)cycloprop-1-ene (1a)† in 90% yield.

^{\dagger} Satisfactory microanalysis data (C, H \pm 0.2% of calculated values) were obtained for all new compounds.

Selected spectroscopic data. (1a): ¹H n.m.r. (300 MHz, CDCl₃) δ 7.0—7.9 (15H, Ph); ¹³C{¹H} n.m.r. (75 MHz, CDCl₃, *J* values in Hz) δ 112.4 (d, J_{FC} 7, CPh(CF=CF₂), 126.0—130.0 (Ph and CF=CF₂), 140.5 (s, PhC=), 154.9 (ddd, J_{FC} 290, 275, 51, CF=CF₂); ¹⁹F n.m.r. (282 MHz, CDCl₃) δ 103.8 (dd, $J_{1,2}$ 31, $J_{2,3}$ 82, F^2), 117.3 (dd, $J_{1,3}$ 115, $J_{2,3}$ 82, F^3), 166.2 p.p.m. (dd, $J_{1,3}$ 115, $J_{1,2}$ 31, F^1); i.r. (hexane) $v_{CF=CF}$ 1784 cm⁻¹.

(3): ¹H n.m.r. (CDCl₃) δ 6.9—7.7 (15H, Ph); ¹⁹F n.m.r. (CDCl₃) δ 88.0 (dd, $J_{2,3}$ 129, $J_{1,2}$ 69, F²), 94.8 (dd, $J_{2,3}$ 129, $J_{1,3}$ 8, F³), 132.5 p.p.m. (dd, $J_{1,3}$ 8, $J_{1,2}$ 69, F¹); i.r. (hexane) v_{CO} 2115, 2054, 2044, 2016 cm⁻¹.

(4): ¹H n.m.r. (CDCl₃) δ 7.1–7.7 (15H, Ph); ¹³C{¹H} n.m.r. (CDCl₃ δ 64.1 [q, J_{FC} 41, $C(CF_3)$], 81.0 (s, CPh), 88.5 (s, CPh), 125.1 (q, J_{FC} 270, CF₃), 128.3–129.6 (Ph), 211.7 (Fe-CO); ¹⁹F n.m.r. (CDCl₃) δ 52.8 p.p.m. (s, CF₃); i.r. (KBr) ν_{CO} 2055, 1997, 1976 cm⁻¹. (5): ¹H n.m.r. (CDCl₃) δ 6.9–7.5 (15H, Ph); ¹⁹F n.m.r. (CDCl₃)

(5): ¹H n.m.r. (CDCl₃) $\circ 6.9$ —7.5 (15H, Ph); ¹9F n.m.r. (CDCl δ 128.6 (d, J_{FF} 13, CF_2), 145.8 p.p.m. (t, J_{FF} 13, CF).

Its hydrocarbon analogue (1b) has been shown previously to react thermally with $[Fe_2(CO)_9]$ to yield the η^4 -cyclohexa-2,4diene complex (2), presumably via a CO insertion reaction of a 1-ferracyclohexa-2,4-diene intermediate.² In contrast, reaction of (1a) with $[Fe_2(CO_9)]$ (20 °C, Et_2O , dark, 5 h) affords the pale yellow η^2 -vinylcyclopropene complex (3)[†] as the major product. The structure of (3) is firmly established by microanalytical and spectroscopic methods. I.r. spectroscopy confirms the presence of an $Fe(CO)_4$ moiety, and the substantial downfield shifts and coupling constant changes of the trifluorovinyl group in the ¹⁹F n.m.r. spectrum confirm that the metal centre is bound to this alkene, by comparison with data reported for other fluoroalkene complexes of the $Fe(CO)_4$ moiety.⁸

In contrast, irradiation of (1a) in the presence of $[Fe_2(CO_9)]$ (20 °C, Et₂O, 24 h) affords the yellow, air stable Fe⁰ complex (4)[†] in 55% yield.⁹ The intermediacy of (3) in this latter reaction is confirmed by its direct photochemical conversion into (4) after irradiation for 14 h. The structure of (4) is also clearly demonstrated spectroscopically, particularly by a singlet CF₃ resonance in the ¹⁹F n.m.r. spectrum, and CF₃ and C-CF₃ carbon resonances coupled as quartets to fluorine in the ${}^{13}C{}^{1}H$ n.m.r. spectrum. As previously observed for the hydrocarbon analogue (1b),¹ irradiation of (1a) in the absence of a transition metal centre leads to the formation of the substituted cyclopentadiene $(5)^{\dagger}$ as the major product. Thermal reaction of (3) in refluxing hexanes (12 h) affords only unco-ordinated (1a) and $[Fe_3(CO)_{12}]$. However there is 19 F n.m.r. evidence of a trace (<5%) of (4) when solutions of (3) are allowed to stand in the dark at room temperature for 24 h. Complex (4) shows no change after 12 h in refluxing hexanes.

These results clearly demonstrate the dramatic change in reactivity of vinylcyclopropenes upon fluorination of the exocyclic alkene. Not only is an η^2 -alkene complex (3) stabilised, but it undergoes no thermal chemistry analogous to its hydrocarbon counterpart. Isolation of such complexes

containing unopened vinylcyclopropenes allows their photochemistry to be examined and contrasted with that of the free ligand. The formation of (4) from (3) proceeds unambiguously by a photochemical pathway since thermal reaction of (3) affords only free (1a), and photolysis of (1a) affords (5). Thus while the photochemistry of free (1a) simply parallels that of its hydrocarbon analogue, binding to iron changes the photochemical pathway dramatically to afford a 4-membered rather than a 5-membered ring.

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