

PREPARATION OF CHLORODIVINYLBORANE TRANSITION METAL COMPLEXES AND THEIR NUCLEOPHILIC SUBSTITUTION AT BORON

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Summary

Chlorodivinyborane (I) prepared in situ from boron trichloride and dimethyldivinyln, reacts under photochemical conditions with ironpentacarbonyl and cyclopentadienyldicarbonylcobalt to give (η^5 -chlorodivinyborane)tricarbonyliron (II) and (η^5 -chlorodivinyborane)cyclopentadienylcobalt (III), respectively, in high yield. Complexes II and III readily undergo base-assisted nucleophilic substitution at boron.

Introduction

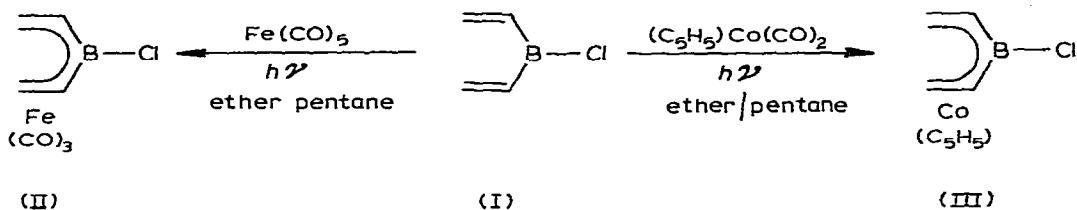
In 1971 we reported the first example of a transition metal complex of a divinyborane derivative: (η^5 -benzyloxydivinyborane)tricarbonyliron (IV) [1]. The ^1H NMR spectrum indicated that benzyloxydivinyborane is present in this complex as a pentahapto ligand, implying a boron—iron bond. Although there have been no further reports of transition metal complexes of acyclic divinyborane derivatives, there have been several recent reports of transition metal complexes of cyclic divinyborane derivatives, including an X-ray crystallographic study which has confirmed the pentahapto nature of divinyborane ligands [2–6]. We now report a convenient high-yield route to substituted acyclic divinyborane transition metal complexes.

Results and discussion

Reaction of boron trichloride with dimethyldivinyln in pentane, followed by removal of dichlorodimethyln gives a solution of chlorodivinyborane (I) [7,8] which is suitable for use in complexation reactions with metal carbonyls.

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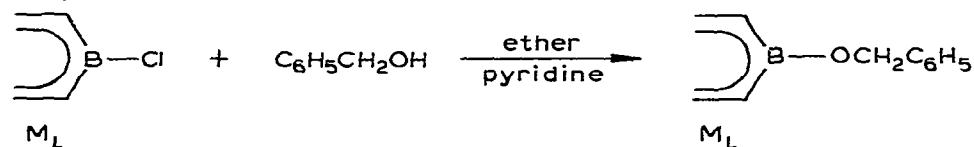
Photolysis of a solution of ironpentacarbonyl and I in 3 : 1 ether/pentane produces (η^5 -chlorodivinyborane)tricarbonyliron (II) in 75% yield.



Although complex II proved to be too labile, due to loss of carbon monoxide, to give a satisfactory elemental analysis, freshly prepared samples were characterized by their NMR, IR, and mass spectra and by transformation into the known complex IV (vide infra).

Photolysis of cyclopentadienyldicarbonylcobalt in the presence of I in 3 : 1 ether/pentane leads to the formation of (η^5 -chlorodivinyborane)cyclopentadienylcobalt (III) in 63% yield based on $(\text{C}_5\text{H}_5)\text{Co}(\text{CO})_2$. Complex III was characterized by elemental analysis and from its NMR and mass spectra. (η^5 -chlorodivinyborane)cyclopentadienylcobalt is a red crystalline solid, m.p. 80°C , which is extremely moisture sensitive, but is stable for a short time in dry air.

Both complexes II and III readily undergo base-assisted nucleophilic substitution at boron to give new substituted divinyborane complexes. Thus treatment of a solution of II, derived from photolysis of I with ironpentacarbonyl (vide supra), with benzyl alcohol and pyridine gives (η^5 -benzyloxydivinyborane)tricarbonyliron (IV) in 54% overall yield.



$\text{M}_L = \text{Fe}(\text{CO})_3, \text{Co}(\text{C}_5\text{H}_5)$

IV ; $\text{M}_L = \text{Fe}(\text{CO})_3$

V ; $\text{M}_L = \text{Co}(\text{C}_5\text{H}_5)$

Analogously treatment of (η^5 -chlorodivinyborane)cyclopentadienylcobalt (III) with one equivalent of benzyl alcohol and pyridine in ether leads to (η^5 -benzyloxydivinyborane)cyclopentadienylcobalt (V), obtained in 87% yield as red crystals, m.p. $43\text{--}44^\circ\text{C}$.

Preliminary experiments show that nucleophilic substitution at boron in complexes such as II and III is a general reaction and can be accomplished with hydride ion, as well as with carbon, nitrogen, and oxygen nucleophiles.

Experimental

All reactions were carried out under nitrogen with rigorous exclusion of moisture.

TABLE 1
¹H NMR OF COMPLEXES II-V^a

Cpd.	C ₆ H ₅	CH ₂	H ₁	H ₂	H _a	C ₅ H ₅	Solvent
II			4.15 (2 H) t (13.1 Hz)	2.73 (2 H) d (12.7 Hz)	1.31 (2 H) d (14.2 Hz)		CS ₂
III			4.05 (2 H) t (13.0 Hz)	2.85 (2 H) d (12.0 Hz)	0.80 (2 H) d (14.0 Hz)	4.28 (5 H) s	C ₆ D ₆
IV ^b	7.0-7.5 (5 H) m	4.94 (2 H) s	3.74 (2 H) t (12.5 Hz)	2.18 (2 H) d (12.0 Hz)	0.80 (2 H) d (14.4 Hz)		C ₆ D ₆
V	7.1-7.8 (5 H) m	5.20 (2 H) s	3.45 (2 H) t (12.4 Hz)	2.82 (2 H) d (11.3 Hz)	0.91 (2 H) d (13.5 Hz)	4.22 (5 H) s	C ₆ D ₆

^a δ, Relative to internal TMS. ^b reported in ref. 1, relative to external TMS.

(η^5 -Chlorodivinyborane)tricarboxyliron (II)

Boron trichloride (3.6 ml, 41 mmol) was added slowly to a stirred solution of dimethyldivinytin (6.4 ml, 40 mmol) in 30 ml of pentane at ca. -40°C. The mixture was allowed to warm to room temperature, and stirring was continued for 3 h. The mixture was then cooled to -78°C, and the pentane solution of chlorodivinyborane was decanted from the dichlorodimethyltin. The dichlorodimethyltin was then washed twice with 10 ml portions of pentane at -78°C. The combined pentane solutions were added to 7 ml of ironpentacarbonyl (52 mmol) in 200 ml of ether. The resulting yellow solution was then photolyzed for 16 h at 10°C with a 150 W medium pressure mercury lamp, followed by solvent removal under high vacuum. The orange residue was extracted with a minimum amount of pentane, and the combined pentane extracts were cooled slowly to -78°C to produce 7.27 g (75%) of (η^5 -chlorodivinyborane)tricarboxyliron. NMR data in Table 1; IR, ν (CO): 2069, 2013, and 1998 cm⁻¹; mass spectrum (70 eV), m/e (relative intensity, assignment): 242 (14, P⁺ ³⁷Cl); 240 (47, P⁺ ³⁵Cl); 212 (69, P - CO⁺); 284 (75, P - 2 CO⁺); 156 (100, P - 3 CO⁺); 56 (61, Fe⁺).

(η^5 -Chlorodivinyborane)cyclopentadienylcobalt (III)

Similarly, a solution of chlorodivinyborane in 30 ml of pentane, prepared from boron trichloride (1.8 ml, 21 mmol) and dimethyldivinytin (3.1 ml, 19 mmol), was added to a solution of cyclopentadienyldicarbonylcobalt (2.0 ml, 14 mmol) in 100 ml of ether and the mixture was photolyzed for 15 h at 10°C. The solvent was then removed under high vacuum and the resulting red residue extracted with a minimum amount of ether. The extract was cooled to -78°C to give 1.26 g of (η^5 -chlorodivinyborane)cyclopentadienylcobalt. Concentration and recooling of the mother liquor produced a second crop of 0.94 g of III to give a total of 2.20 g (69%), m.p. 80°C. (Found: C, 47.96; H, 4.64. C₉H₁₁BClCo calcd.: C, 48.19; H, 4.49%). NMR data in Table 1; mass spectrum (70 eV), m/e (relative intensity, assignment): 226 (38, P⁺ ³⁷Cl); 224 (81, P⁺ ³⁵Cl); 188 (20, P - HCl⁺); 124 (100, C₅H₅Co⁺); 59 (62, Co⁺).

(η^5 -Benzoyloxydivinyborane)tricarboxyliron (IV)

To (η^5 -chlorodivinyborane)tricarboxyliron, prepared in situ as above, from

boron trichloride (0.90 ml, 10.0 mmol), dimethyldivinyltin (1.60 ml, 10.0 mmol) and ironpentacarbonyl (1.40 ml, 10.4 mmol) in 300 ml of 3 : 1 ether/pentane, was added dropwise a solution of benzyl alcohol (1.04 ml, 10.0 mmol) and pyridine (0.88 ml, 11.0 mmol) in 3 ml of ether. The mixture was stirred at room temperature for 0.5 h. The solution was filtered to remove the resulting pyridine hydrochloride, and the solvent removed under high vacuum. The oily orange residue was extracted with 15 ml of pentane. The pentane solution was filtered through a small amount of alumina (7% H₂O deactivated), and cooled slowly to -78°C. The pentane was decanted and the resulting red oil dried under high vacuum to give 1.69 g (54%) of (η^5 -benzyloxydivinylborane)-tricarbonyliron. A sample for elemental analyses was obtained by high vacuum distillation. (Found: C, 53.70; H, 4.27; Fe, 17.89. C₁₄H₁₃BF₃O₄ calcd.: C, 53.91; H, 4.20; Fe, 17.90%.

(η^5 -Benzyloxydivinylborane)cyclopentadienylcobalt (V)

A solution of benzyl alcohol (0.094 ml, 0.91 mmol) and pyridine (0.075 ml, 0.93 mmol) in 2 ml of ether was added dropwise to a stirred solution of (η^5 -chlorodivinylborane)cyclopentadienylcobalt (0.208 g, 0.93 mmol) in 10 ml of ether at room temperature. Immediate precipitation of pyridine hydrochloride occurred. After stirring for a further 5 min, the mixture was filtered through a 3 × 1 cm plug of alumina (7% H₂O deactivated) and the resulting clear solution was concentrated under vacuum to a volume of 2 ml, 1 ml of hexane was added, and the resulting solution cooled slowly to -78°C. Filtration gave 0.2324 g (87%) of (η^5 -benzyloxydivinylborane)cyclopentadienylcobalt, m.p. 43–44°C. (Found: C, 64.76; H, 6.29; Co, 20.09. C₁₆H₁₈BCoO calcd.: C, 64.91; H, 6.13; Co, 19.91%). NMR data in Table 1; mass spectrum (70 eV), *m/e* (relative intensity, assignment): 296 (22, P⁺); 188 (10, P - C₆H₅CH₂OH⁺); 161 (24, (C₅H₅)Co(C₂H₂B)⁺); 124 (42, C₅H₅Co⁺); 108 (98, C₆H₅CH₂OH⁺); 107 (83, C₆H₅CH₂O⁺); 91 (100, C₇H₇⁺); 77 (66, C₆H₅⁺); 59 (15, Co⁺).

Acknowledgement

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