Table I. Spectral Data for the Carbamoylborane Cyclic Dimer and the Carbamoylborane Adduct of *N*-Methylmorpholine

type		$[BH_2C(O)NHC_2H_5]_2$	$O(CH_2CH_2)_2N(CH_3)BH_2C(O)NHC_2H_5$
infrared[a]	(N—H)	3410	3440, 3360
	(B—H)	2400	2369
	(amide I, C=O)	1570	1595
	(amide II, N—H)	1520	1477
^{11}B NMR[b]		-8.6 (t, J_{BH} = 95 Hz)	-9.9 (t, J_{BH} = 97 Hz)
^{1}H NMR[b]	N-CH_2CH_3	1.18 (t, J_{HCCH} = 7.5 Hz)	1.09 (t, J_{HCCH} = 7.4 Hz)
	N-CH_2CH_3	3.38 (m, J_{HCCH} = 7.5 Hz, J_{HNCH} = 5.7 Hz)	3.24 (m)
	N-H	6.42 (b s)	5.7 (b s)
	N-CH_3		2.88 (s)
	ring-H		2.85 (m), 3.49 (m), 3.75 (m)
			4.03 (m)
^{13}C NMR[b]	N-CH_2CH_3	13.51 (s)	14.98 (s)
	N-CH_2CH_3	33.75 (s)	31.70 (s)
	N-CH_3		48.85 (s)
	O-CH_2CH_2-N		57.63 (s)
	O-CH_2CH_2-N		61.18 (s)

[a] All spectra were taken as $CHCl_3$ solutions. [b] Key: s = singlet; m = multiplet; t = triplet; b = broad.

formation. The reasons for this are currently being studied. The structure of the cyclic dimer can be considered to be analogous to the cyanoborane oligomer that is formed from $[BH_3CN]^-$ in the presence of an acid.[15]

Infrared, ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, and mass spectral data support the proposed formulation for the cyclic dimer (Figure 1). The infrared spectrum exhibits absorptions characteristic of C=O, N—H, and B—H moieties. The assignments have been made based on the corresponding spectra of the cyanoborane cyclic oligomer ($[BH_2CN]_x$),[15] the (*N*-ethylcarbamoyl)borane adducts of several trialkylamines,[2,13,16] and the generally accepted assignments for organic amides.[17] The B-H stretching mode of the (*N*-ethylcarbamoyl)borane adduct of *N*-methylmorpholine is reported at 2369 cm^{-1}, which is consistent with solution spectra of other trialkylamine adducts. The shift to higher energy, 2400 cm^{-1}, of the B-H stretching mode in the cyclic dimer is consistent with the change observed when the amine of the (*N*-ethylcarbamoyl)borane is changed from a trialkylamine (2330 cm^{-1}) to a dialkylamine (2365 cm^{-1});[2] this may be attributed to analogous inductive effects occurring in the two systems. The N-H stretching mode in the *N*-methylmorpholine–carbamoylborane adduct exhibits two bands, which suggests some degree of intermolecular hydrogen bonding.[17] However, the shift to higher frequency of the N-H stretching mode, 3410 cm^{-1}, in the dimer ring suggests an absence of intermolecular hydrogen bonding.

In the *N*-methylmorpholine adduct the amide I and amide II bands are observed at 1595 and 1477 cm^{-1} respectively, consistent with solution spectra obtained on other trialkylamine adducts. In contrast, the amide I and amide II bands of the dimer are observed at 1570 and 1520 cm^{-1}. The shift to higher wavenumber of the amide II band corresponds to the dimer structure in that the N-H bond length would be expected to decrease since the lone pair on the amide is bonded to the boron. The shift to lower energy of the C=O mode implies a decrease in partial positive charge on the carbon and a lengthening of the carbon–oxygen bond resulting from the relative increase in electron density on the boron (and concurrent increase in the B-H frequency).

The ^{11}B NMR data for both the *N*-methylmorpholine adduct and the cyclic dimer correlate well with previously reported spectra.[12] Each triplet indicates the presence of a BH_2 moiety (with comparable coupling constants) while the proton-decoupled spectra exhibit only a single resonance, indicating the presence of a single type of boron in each compound.

The ^{1}H and $\{^{1}H\}^{13}$C NMR spectra of the *N*-methylmorpholine adduct show absorptions similar to those reported for other (*N*-ethylcarbamoyl)boranes (e.g. pyridine[13] and trimethylamine[2]) with peaks attributable to the *N*-ethyl group and the N-H on the carbamoyl function. The *N*-ethyl resonances in the ^{13}C NMR of the ring compound correspond to those observed for carbamoylborane adducts.

The mass spectral data for the ring compound, exhibiting no mass higher than 169, supports the assignment of a cyclic dimer structure rather than a linear oligomeric structure. The peak clusters and their relative intensities are what would be expected from the natural abundance of the boron isotopes.

A ring resulting from boron coordination to the carbonyl oxygen atom would be expected to have an IR absorption corresponding to the C=N$^+$R and also a ^{11}B NMR shift downfield of that observed. On this basis, the latter structure can be eliminated.

The reaction of the dimer with methylamine supports the ring formulation since no other product other than the known methylamine–carbamoylborane is generated. Additionally, this result indicates that use of the rings offers potential for formation of primary and secondary amine carbamoylboranes at rates faster than reported exchange reactions.[2] For example, exchange between methylamine and the carbamoylborane adduct of trimethylamine showed the reaction to be slower, being 65% complete in 1 week.[2] Similar reactivity studies are currently underway to establish the synthesis and reactivity of dimers containing different alkyl groups with amino acids and (aminomethyl)phosphonates.

Acknowledgment. Support of this work by the Utah Agricultural Experiment Station, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and a Sigma Xi Grant-In-Aid (D.A.F.) is gratefully acknowledged.

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Preparation of Monosubstituted Borane Adducts of an NH-Containing (Aminomethyl)phosphonate

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Received October 9, 1990

Introduction

Initially, the purpose of making a number of boron compounds that were analogues of amino acids was for use in boron neutron capture therapy.[1] However, since the compounds themselves

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0020-1669/91/1330-2434$02.50/0

turned out to be biologically active,[2] an increasing interest in the synthesis[3] and biological activity[4] of amine·BH_2X compounds (X = CN, CONHR, COOR, C(OR)=NR, etc.) has been revealed by a number of reports in recent years. We recently reported synthesis and characterization of monosubstituted borane adducts of ((dialkylamino)methyl)phosphonate.[5] In view of the higher biological activity of some NH-containing amine·BH_2X adducts,[4b,6] we initiated studies on the preparation of (aminomethyl)-phosphonate–borane derivatives, $(RO)_2P(O)CH_2NHCH_3\cdot BH_2X$ (X = CN, CONHEt, COOH, COOEt) in which nitrogen contains at least one hydrogen. The results of these studies are reported in this paper.

Experimental Section

Materials. All glass equipment was oven-dried at 120 °C and assembled under a stream of dry nitrogen gas. Triethyloxonium tetrafluoroborate was prepared according to the procedure of Meerwein.[7] An approximately 1 M solution of Et_3OBF_4 in CH_2Cl_2 was used as a fresh solution. The $(BH_2CN)_n$ oligomer was prepared according to a reported method;[8] at no time was the oligomer handled dry because of the potential explosion hazard.[9]

Pyridine·BH_2X (X = COOH, CONHEt, C(OMe)=NEt, COOMe) adducts were prepared according to published methods.[3i] The compounds $O(CH_2CH_2)_2NCH_3\cdot BH_2COOH$ and $O(CH_2CH_2)_2NCH_3\cdot BH_2CONHEt$ were prepared by a known method,[3b] but with modifications described from this laboratory,[3i] in 71% (lit. 41%) and 61% yield, respectively. In the preparation of $O(CH_2CH_2)_2NCH_3\cdot BH_2CNEtBF_4$ 2 equiv of Et_3OBF_4 was used. In an adaptation of our earlier reported procedure,[3i] the compounds $O(CH_2CH_2)_2NCH_3\cdot BH_2C(OEt)=NEt$ and $O(CH_2CH_2)_2NCH_3\cdot BH_2COOEt$ were prepared in 54% and 37% yields, respectively. The (aminomethyl)phosphonate $(iPrO)_2P(O)CH_2NHCH_3$ was prepared by adapting a reported method[10] with minor modification.

The ^1H and ^{13}C NMR spectra were obtained on a Varian XL-300 spectrometer using TMS as an internal standard. The ^{31}P and ^{11}B NMR spectra were recorded on a JEOL FX-90Q instrument with the chemical shifts reported relative to 85% H_3PO_4 and $BF_3\cdot OEt_2$, respectively. The IR spectra were run on a Perkin-Elmer 1750 FT spectrometer by taking a $CDCl_3$ solution of the sample between NaCl disks. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ.

Preparation of $(iPrO)_2P(O)CH_2NHCH_3\cdot BH_2CN$ (1). To a sample of $(BH_2CN)_n$ oligomer (0.2 g, 5 mmol) in 50 mL of CH_2Cl_2 was added $(iPrO)_2P(O)CH_2NHCH_3$ (1.05 g, 5 mmol), and the mixture was stirred for 2 h at room temperature. Monitoring of the reaction mixture by ^{31}P NMR showed complete conversion of the (aminomethyl)phosphonate to cyanoborane adduct. The CH_2Cl_2 was removed and ether (50 mL) was added to the residue. The solution, which also contained some insoluble fluffy material, was treated with activated charcoal and filtered to give a clear colorless solution. Ether was removed, and the resultant thick oil was triturated with hexane to give a white solid: yield 1.14 g (92%); mp 55–57 °C. Anal. Calcd for $C_9H_{22}BN_2O_3P$: C, 43.58; H, 8.94; N, 11.29, Found: C, 43.72; H, 8.83; N, 11.31.

Preparation of $(iPrO)_2P(O)CH_2NHCH_3\cdot BH_2CONHEt$ (2). A mixture of $(iPrO)_2P(O)CH_2NHCH_3$ (6.52 g, 31.2 mmol) and $O(CH_2CH_2)_2NCH_3\cdot BH_2CONHEt$ (3.86 g, 20.8 mmol) was stirred at room temperature for 4 days. Hexane (80–100 mL) was added to the reaction mixture, which was then cooled at −10 °C for 48 h to give a light yellow solid. The hexane solution was decanted, and the solid was dissolved in ether, treated with activated charcoal, and filtered to give a clear colorless solution. Fresh hexane was added to this solution until light turbidity appeared, which disappeared on warming. The solution was cooled at −10 °C to give a white solid, which was filtered and washed with hexane. The mother liquor on concentration and cooling gave an additional amount of solid: total yield 4.9 g (80%); mp 59–61 °C. Anal. Calcd for $C_{11}H_{28}BN_2O_4P$: C, 44.92; H, 9.59; N, 9.52. Found: C, 44.75; H, 9.36; N, 9.21.

Preparation of $(iPrO)_2P(O)CH_2NHCH_3\cdot BH_2COOH$ (3). A sample of $(iPrO)_2P(O)CH_2NHCH_3$ (3.14 g, 15 mmol) was mixed with $O(CH_2CH_2)_2NCH_3\cdot BH_2COOH$ (1.6 g, 10 mmol) and stirred at room temperature for 6 days. The reaction mixture was dissolved in CH_2Cl_2, treated with activated charcoal, and filtered to give a clear colorless solution. The solution was concentrated to a small volume, ether was added, and the mixture was cooled to give a white crystalline material, which was filtered and washed with ether. The mother liquor on concentration and cooling gave an additional amount of solid: total yield 2.5 g (93%); mp 96–98 °C. Anal. Calcd for $C_9H_{23}BNO_5P$: C, 40.47; H, 8.68; N, 5.24. Found: C, 40.21; H, 8.49; N, 5.16.

Preparation of $(iPrO)_2P(O)CH_2NHCH_3\cdot BH_2COOEt$ (4). A reaction mixture of $(iPrO)_2P(O)CH_2NHCH_3$ (1.0 g, 4.8 mmol) and $O(CH_2CH_2)_2NCH_3\cdot BH_2COOEt$ (0.6 g, 3.2 mmol) was stirred for 6 days at room temperature. The solution was dissolved in ether, treated with activated charcoal, and filtered. Solvent removal gave a colorless oil, which was dissolved in hexane and cooled at −10 °C for 48 h. A white crystalline solid separated at the bottom, leaving excess free (aminomethyl)phosphonate in hexane solution, which was decanted; the residue was washed twice with cold hexane and dried under vacuum. The mother liquor on concentration and cooling gave an additional amount of solid: total yield 0.75 g (80%); mp 54–56 °C. Anal. Calcd for $C_{11}H_{27}BNO_5P$: C, 44.77; H, 9.22; N, 4.74; Found: C, 44.85; H, 9.00; N, 4.75.

Results and Discussion

The cyanoborane adduct of diisopropyl ((methylamino)-methyl)phosphonate (**1**) was readily prepared by using an earlier reported method[5a] in 93% yield by allowing $(iPrO)_2P(O)CH_2NHCH_3$ to react with $(BH_2CN)_n$ oligomer. The cyanoborane adduct was alkylated with Et_3OBF_4 to give the nitrilium salt, $(iPrO)_2P(O)CH_2NHCH_3\cdot BH_2CNEtBF_4$. The IR of the nitrilium salt showed an absorption at 2317 cm^{-1} for $C{\equiv}NEtBF_4$ along with the characteristic B—H (2440 and 2470 cm^{-1}) and P=O (1227 cm^{-1}) absorptions. However, neither carbamoylborane **2** nor carboxyborane **3** could be obtained in reasonable yields on alkaline and acidic hydrolysis of the nitrilium salt, respectively. Previous reports[3b] indicate that alkaline or acidic hydrolysis of nitrilium salts of NH-containing amine cyanoboranes to give carbamoyl or carboxyborane derivatives were unsuccessful. Our attempts using similar procedures have produced both products, but the yields have been poor (10%) and because free amine is generated the systems are very difficult to handle. Spielvogel has reported the use of base-exchange reactions[11] for the preparation of NH-containing amine–carbamoyl–carboxy-, and -alkoxycarbonylboranes. The method involves an excess of NH-containing amine (eg. Me_2NH, $MeNH_2$, and NH_3) reacting with $Me_3N\cdot BH_2X$ (X = CONHEt, COOH, COOR). When we adapted this method for the preparation of **2–4**, the reaction times were typically long (2 weeks) for completion of 50% of the reaction (^{31}P NMR), and purification was difficult. In order to reduce the length of reaction times and to overcome difficulty in purification, we have used monosubstituted borane adducts of some weaker tertiary amines such as pyridine and *N*-methylmorpholine.

From the pK_a values of trimethylamine (9.80), *N*-methylmorpholine (7.13), and pyridine (5.17), it was assumed that their

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Table I. Exchange Reaction between Amine·BH_2X and $(iPrO)_2P(O)CH_2NHCH_3$ to give $(iPrO)_2P(O)CH_2NHCH_3·BH_2X$

amine·BH_2X	time/ days	% conversion[a] to $(iPrO)_2P(O)CH_2NHCH_3·BH_2X$ X = CONHEt	X = COOH	X = COOEt	% isolated yields
$Me_3N·BH_2X$	8	53	41	54	
	16	58	50	70	30–50
$C_5H_5N·BH_2X$	8	80	45	70	
	16	85	50	77	35–70
$O(CH_2CH_2)_2NCH_3·BH_2X$	4–6	100	100	100	80–93

[a] Percent conversion is based on the ^{31}P NMR integration values of the reaction mixture.

Table II. Spectroscopic (IR, ^{11}B NMR, and ^{31}P NMR) Data for Borane Derivatives of Diisopropyl ((Methylamino)methyl)phosphonate[a]

compd	IR ($CDCl_3$) ν, cm^{-1}	^{11}B NMR ($CDCl_3$) δ, ppm	^{31}P NMR ($CDCl_3$) δ, ppm
1	1237 (P=O), 2198 (C≡N) 2411 (B—H), 3092 (N—H)	−16.4 (t, br)	17.3
2	1244 (P=O), 1578 (C=O) 2375 (B—H), 3113 (N—H) 3347 (N—H)	−9.3 (t, br)	17.6
3	1245 (P=O), 1648 (C=O) 2396 (B—H), 3113 (N—H)	−11.2 (t, br)	18.1
4	1242 (P=O), 1657 (C=O) 2390 (B—H), 3123 (N—H)	−12.1 (t, br)	19.8

[a] Key: t = triplet; br = broad.

Table III. ^1H NMR ($CDCl_3$) Spectral Data for Borane Derivatives of Diisopropyl ((Methylamino)methyl)phosphonate[a]

compd	δ, ppm
1	1.38 (m, $OCH(CH_3)_2$), 2.74 (d, NCH_3), 2.94 (m, $PCHH$), 3.24 (m, $PCHH$), 4.80 (m, $OCH(CH_3)_2$), 6.10 (s, br, NH)
2	1.11 (t, NCH_2CH_3), 1.37 (m, $OCH(CH_3)_2$), 2.71 (d, NCH_3), 2.90 (m, $PCHH$), 3.20 (m, $PCHH$), 3.30 (m, NCH_2CH_3), 4.80 (m, $OCH(CH_3)_2$), 5.24 (s, br, $NHCH_3$), 5.47 (s, br, C(O)NHEt)
3	1.36 (m, $OCH(CH_3)_2$), 2.76 (d, NCH_3), 2.95 (m, $PCHH$), 3.37 (m, $PCHH$), 4.80 (m, $OCH(CH_3)_2$), 4.90 (s, br, NH), 9.60 (s, br, COOH)
4	1.24 (t, $COOCH_2CH_3$), 1.37 (m, $OCH(CH_3)_2$), 2.77 (d, NCH_3), 2.94 (m, $PCHH$), 3.34 (m, $PCHH$), 4.08 (q, $COOCH_2CH_3$), 4.65 (s, br, NH), 4.80 (m, $OCH(CH_3)_2$)

[a] Key: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad.

BH_2X adducts should undergo exchange reactions in the order pyridine·BH_2X > *N*-methylmorpholine·BH_2X > trimethylamine·BH_2X, reflecting the increasing basicity of the amine and thus a stronger acid–base adduct. The exchange reactions (Scheme I) were carried out by using 1.5 equiv of $(iPrO)_2P(O)CH_2NHCH_3$ with amine·BH_2X adducts as neat solutions. Results of the exchange reactions with these three tertiary amine·BH_2X adducts are shown in Table I. Exchange reactions with $Me_3N·BH_2X$ are much slower, consistent with the higher pK_a value of Me_3N. However, *N*-methylmorpholine·BH_2X adducts undergo more facile exchange reactions than pyridine·BH_2X adducts, though pyridine is a weaker base than *N*-methylmorpholine. From the order of the observed displacement reactions $O(CH_2CH_2)_2NCH_3·BH_2X > C_5H_5N·BH_2X > Me_3N·BH_2X$, it appears that not only the basicity of the amine but also the geometry of its borane adduct may be involved in determining the extent of base displacement. Isolation of products is also favored for the morpholine adducts. In the exchange reactions with $Me_3N·BH_2X$ and $C_5H_5N·BH_2X$ adducts, the purification requires column chromatography, resulting in lower isolated yields of the products, $(iPrO)_2P(O)CH_2NHCH_3·BH_2X$ (30–50% with $Me_3N·BH_2X$ and 35–70% with $C_5H_5N·BH_2X$). However, purification of the products from exchange reactions with $O(CH_2CH_2)_2NCH_3·BH_2X$ was easy, since the reaction is quantitative. Purification involves only washing the excess free (aminomethyl)phosphonate and the byproduct *N*-methylmorpholine with nonpolar solvents, giving higher isolated yields (80–95%). No noticeable exchange reaction was observed with imino ether borane derivatives of these three amines even after long reaction times (3 weeks). It appears that the absence of a carbonyl group adjacent to the boron in the imino ether may be responsible for its lack of an exchange reaction. When the carbonyl group is present, the partial negative charge on boron is diminished, resulting in facile approach by the lone pair of nitrogen on the attacking amine. In the imino ether derivative, apart from steric factors which may be present, the absence of a carbonyl group adjacent to boron causes no decrease in negative charge. Consequently, the approach of the nitrogen with its lone pair to the boron is less favored (even though a weaker B–N bond is expected in the imino ether).

Scheme I

$$\text{amine·}BH_2X + (iPrO)_2P(O)CH_2NHCH_3 \rightarrow \text{amine} + (iPrO)_2P(O)CH_2NHCH_3·BH_2X$$

$$\text{amine} = Me_3N,\ C_5H_5N,\ O(CH_2CH_2)_2NCH_3$$

$$X = \text{CONHEt, COOH, COOR, C(OR)=NEt}$$

All the compounds are characterized by IR and ^{11}B, ^{31}P, ^1H, and ^{13}C NMR spectroscopy (Table II–IV) and elemental analysis. In the IR, all compounds show absorption in the regions at 3092–3123, 2375–2411, and 1237–1245 cm^{-1} for N—H, B—H, and P=O, respectively. Characteristic carbonyl absorptions for acid, amide, and ester are observed (Table II).

^{11}B NMR spectra for all compounds show very broad triplets characteristic of BH_2 moieties in these types of compounds.[5b] These broad triplets collapse to sharp singlets on proton decoupling, indicating each compound contains only one type of boron moiety. The ^{31}P NMR signals for these compounds (Table II) are upfield by 5–6 ppm from free (aminomethyl)phosphonate, which is comparable in magnitude to that observed when the parent phosphonate is compared to its HCl salt.[12] The ^1H NMR data

Table IV. ^{13}C NMR Spectral Data for Borane Derivatives of Diisopropyl ((Methylamino)methyl)phosphonate[a]

compd	δ, ppm (J, Hz) POC*C*	POC*C*	PC	NC	NC*C*	NC*C*	COC*C*	COC*C*
1	23.9 (m)	72.4 (d, J_{POC} = 7.2) 73.0 (d, J_{POC} = 6.7)	51.0 (d, J_{PC} = 152.8)	41.6 (d)				
2	23.9 (d) 24.0 (d)	71.9 (d, J_{POC} = 6.6)	51.3 (d, J_{PC} = 148.5)	41.5 (s)	32.4 (s)	15.2 (s)		
3	23.0 (m)	72.4 (d, J_{POC} = 6.6) 72.1 (d, J_{POC} = 6.9)	51.7 (d, J_{PC} = 149.0)	41.6 (d)				
4	25.3 (m)	72.3 (d, J_{POC} = 6.9) 72.1 (d, J_{POC} = 6.6)	51.4 (d, J_{PC} = 148.5)	41.7 (s)			56.9 (s)	16.0 (s)

[a] Key: s = singlet; d = doublet; m = multiplet.

(Table III) are consistent with those expected from the structural assignment for these compounds. Methyl and methyne moieties of the isopropoxy groups show a multiplet and complex multiplet, respectively, indicating inequivalency of the isopropoxy groups and coupling with phosphorus. The P–CH_2 group exhibits two complex multiplets in these compounds, revealing that the two protons are not equivalent and each of them couples geminally as well as to an NH proton and the phosphorus atom. When the NH proton was irradiated, the two complex multiplets collapsed to two triplets. The methyl group of the amine moiety gives a doublet due to coupling to the NH proton. Irradiation of the NH proton resulted in the collapse of this doublet to a single peak.

The ^{13}C NMR (Table IV) further confirms the inequivalency of the isopropoxy groups by exhibiting a multiplet for the methyl carbons. The methyne carbons exhibit two doublets (except for **2**, which shows a doublet), indicating two different environments for the isopropoxy group. The large value for the P–C coupling is consistent for these types of compounds.[5b] Appearance of a doublet for the NCH_3 carbon in compounds **1** and **3** may be due to either long-range coupling with phosphorus or the diastereoscopic nature. Chemical shifts of other carbon moieties are consistent with the structures for these compounds.

Acknowledgment. We acknowledge the support of this research by the Utah Agricultural Experiment Station of Utah State University and the donors of the Petroleum Research Fund, administered by the American Chemical Society. We thank Dr. M. L. Ettel for her help in preparing the (aminomethyl)-phosphonate.

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Nature of the Catalytically Inactive Cobalt Hydride Formed upon Hydrogenation of Aromatic Substrates. Structure and Characterization of the Binuclear Cobalt Hydride $[\{Pr^i_2P(CH_2)_3PPr^i_2\}Co]_2(H)(\mu\text{-}H)_3$

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Received July 23, 1990

The homogeneous, catalytic hydrogenation of aromatic rings still remains a curiosity despite the work reported in the literature.[4] This is largely due to the fact that forcing conditions and poor turnovers have limited the applicability of these systems even though reported stereoselectivities are much higher than in conventional heterogeneous systems. Cobalt-derived catalysts are a good case in point. Complete cis stereoselectivity is observed for the hydrogenation of benzene at 0–20 °C and 1 atm H_2 pressure using $(\eta^3\text{-}C_3H_5)Co[P(OMe)_3]_3$ or $(\eta^3\text{-}C_8H_{13})Co[(C_6H_{11})_2P(CH_2)_3P(C_6H_{11})_2]$, but turnover numbers are extremely low, ranging from 10 to 100 mol of substrate/mol of catalyst before the formation of catalytically inert mono-[5] or polynuclear hydrides,[6] respectively. Our interest in the related polynuclear hydrides of rhodium[7] such as $[(dippp)Rh]_2(\mu\text{-}H)_2$ (dippp ≡ 1,3-bis(diisopropylphosphino)propane) was incentive to examine the nature of the catalytically inactive cobalt hydride formed during the hydrogenation of arenes using the cobalt catalyst precursor $(\eta^3\text{-}C_3H_5)Co(dippp)$ (**1**). It is interesting to note that the analogous rhodium–allyl complex, $(\eta^3\text{-}C_3H_5)Rh(dippp)$, reacts with H_2 to form the binuclear dihydride $[(dippp)Rh]_2(\mu\text{-}H)_2$ with no evidence of hydrogenation of aromatic substrates.[7] In this report, we describe the characterization of a dark blue cobalt hydride complex that is isolated from the catalytic hydrogenation of aromatic substrates.

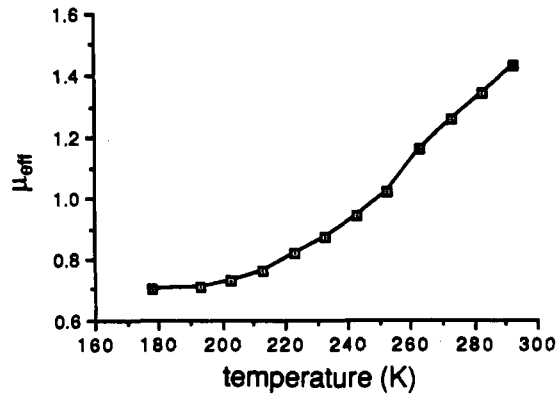
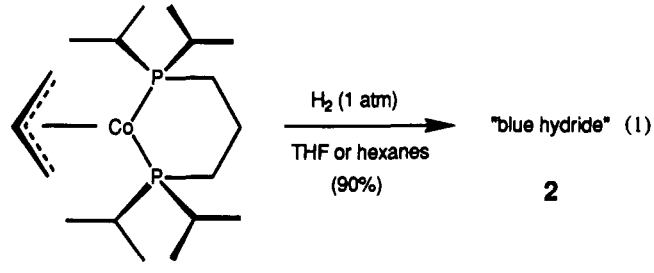


Figure 1. Temperature dependence of μ_{eff} for $[(dippp)Co]_2(H)(\mu\text{-}H)_3$ (**2**) between +20 and −95 °C.

The purple cobalt–allyl derivative **1** serves as a catalyst precursor for the hydrogenation of benzene at 0 °C and ≤1 atm H_2 pressure, generally producing 10–30 equiv of cyclohexane before H_2 uptake is slowed and the catalyst solution turns to a deep, dark blue color. The blue hydride **2** can be isolated from this solution, but it can also be synthesized independently in high yield by stirring a solution of the allyl derivative **1** in a nonaromatic solvent such as THF or hexanes under H_2 at room temperature (eq 1). This blue hydride does not act as a catalyst for the hydrogenation of benzene.



The blue hydride **2** shows paramagnetic behavior in solution at 20 °C (μ_{eff} = 1.4 ± 0.1 μ_B (Evan's method)[8]); however, when it is cooled to −95 °C, its ^1H NMR spectrum appears to be that of a diamagnetic compound, particularly since the resonances for the dippp ligand appear in their typical positions. Unfortunately, only very broad, featureless peaks could be discerned in the hydride region. Interestingly, as the temperature is lowered, the magnetic susceptibility also decreases until a value for μ_{eff} of 0.7 μ_B at −95

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