

While these observations rule out predissociation of methoxide, three kinetically indistinguishable mechanisms for the overall conversion of 1 to 2 must still be considered. They are (Scheme I) (I) precoordination of CO to 1 followed by insertion of CO into the metal-oxygen bond of A, (II) an unprecedented concerted insertion of CO into the metal-oxygen bond, and (III) the displacement of methoxide by CO to form charged intermediates B, which may revert to starting materials or be converted to product 2.

When 1 was combined with ^{13}C O from -20 to -100 °C, a very broad single resonance was observed at 184 ppm in the ^{13}C NMR spectrum, suggesting some pre-equilibrium interaction of 1 and ^{13}C O takes place prior to forming 2. During this apparently rapid process, no loss of ^{195}Pt coupling to either the methoxide protons or the DPPE phosphorous nuclei is observed.

Consistent with this observation, when related complex 3 was combined with ^{13}C O under the same conditions, two resonances were observed which correspond to free ^{13}C O and a new complex of 3 and ^{13}C O as evidenced by ^{195}Pt satellites.⁷ The new complex shows no large ^{31}P to ^{13}C coupling, and the two methoxide groups remain equivalent by ^1H NMR.⁸ Warming the solution changes the distribution⁹ of these signals in favor of free CO until at -20 °C the two signals coalesce making further quantification impossible. Together these observations suggest the first step of carbonylation may be pre-equilibrium coordination of CO to form intermediate A.

While dissociation of methoxide from 1 is clearly very slow, the same cannot be assumed for A. In order to determine the molecularity of the overall carbonylation reaction, a crossover experiment was carried out in which 1 was combined with 15 equiv of CD_3OD and 10 atm of CO; NMR analysis of product 2 showed less than 5% OCD_3 groups. Independent measurements of the carbonylation and methanol exchange rates of 1⁶ and the crossover dependence on CO pressure¹⁰ suggest that even this small amount of observed crossover is accounted for by exchange of 1 and CD_3OD . To the accuracy of our experiments, this result shows methoxide does not dissociate from 1 at any time during carbomethoxide synthesis and we suggest the same may be true for 3 and 5.¹¹ Together these observations show CO can coordinate to platinum(II) alkoxides in preequilibrium fashion which can be followed by a rate-limiting inner-sphere insertion of CO into an available metal-oxygen bond.¹²

(6) Pseudo-first-order exchange of 10 equiv of CD_3OD with 1 and 3 shows $-d[\text{PtOCH}_3]/dt = k[\text{PtOCH}_3][\text{CD}_3\text{OD}]$; this result requires non-dissociative methanol exchange with the error in the intercept of a k_{obsd} vs. $[\text{CD}_3\text{OD}]$ plot corresponding to the maximum rate of methoxide dissociation. For both 1 and 3, this rate is less than 10^{-7} s $^{-1}$. While methoxide dissociation from 1 is more than 10^8 slower than the rate of carbonylation, overall methanol exchange is only a factor of 9 slower than carbonylation at 5 atm of CO pressure.

(7) ^{13}C parameters ($\text{CD}_2\text{Cl}_2/\text{CH}_2\text{Cl}_2$) at -80 °C: 184.9 (s) ppm; $J_{\text{CPT}} = 175.3$ Hz; line width = 17 Hz.

(8) These observations suggest a square-pyramidal ground state with apical CO for the five-coordinate CO adduct.

(9) Thermodynamic parameters measured: $\Delta H^\ddagger = -7.4 \pm 0.1$ kcal/mol, $\Delta S^\ddagger = -26 \pm 3$ eu. Temperature range: -75 to -25 °C.

(10) Crossover was determined by integration of CH_3OD vs. $\text{PtCO}_2\text{C}_2\text{H}_5$ resonances (accuracy of the reported figure is 5% +0, -2%). At lower CO pressures, larger extents of crossover is noted (12% at 5 atm). The crossover dependence on $[\text{DOCD}_3]$ and on CO pressure shows that, within our experimental error, carbonylation is a completely intramolecular insertion process from A.

(11) Because associative methanol exchange is faster than associative carbonylation for 3, similar crossover experiments could not be run with this complex. However, the similarity of carbonylation kinetics and methanol exchange for 1 and 3 suggest the mechanism of carbonylation of 3 and 5 are similar to that investigated for 1. NMR and X-ray crystallographic data show 1 and 3 are very similar, structurally.

Several interesting aspects are worth mentioning. In complex 1, CO inserts into the Pt-O bond without our ever observing insertion into the available Pt-C bond in the same molecule.¹³ Similarly, in complex 5 the second metal-oxygen bond reacts with CO in preference to the available sp^2 metal-carbon bond. This second carbonylation is faster than the first as 5 never builds up to more than a few percent during this reaction.¹⁴

This insertion mechanism is analogous to those previously established for insertion of CO into metal-carbon bonds;¹⁵ it demonstrates that outer sphere processes need not be invoked to explain the reactions of late transition metal-oxygen bonds.¹⁶ The implications of these results to the overall mechanism of oxalate ester synthesis will be reported elsewhere as will the general implications of these results to the reactivity of late transition metal-carbon, -nitrogen, and -oxygen bonds.

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Registry No. 1, 82405-05-8; 2, 91993-69-0; 3, 97295-81-3; 4, 97295-82-4; 5, 97295-83-5; (DPPE)PtCH₃(OCH₃)(CO), 97295-84-6; CO, 630-08-0.

(12) Our experiments cannot distinguish between the involvement of a polar M-O bond and a contact ion pair in A, the difference between which is more semantic than practically significant. Since any charge separation along the reaction coordinate must be so transient as to exclude the faster than diffusion controlled deuteron scrambling with CD_3OD solvent, we think of this reaction as involving a polar transition state. Clearly OR ligands do not leave the Pt coordination sphere during insertion prior to actual O-C bond formation. This situation is analogous to the generally accepted mechanism for alkyl migration to coordinated CO; polar M-C bonds do, at some point, break as new C-C bonds form. Other experiments show similar five-coordinate (DPPE)PtR(OCH₃)-(CH₃OH) complexes (R = CH₃, OCH₃) fail to react with esters or ethylene oxide in THF/methanol solutions. This suggests ion pairs are not accessible in these systems.

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(14) No evidence for an α,β -dicarbonyl product is seen. To the contrary, in other systems the decarbonylation of such species is rapid. In addition, the importance of bis(carbomethoxide) complexes in the synthesis of oxalate esters by Pd catalysts is inferred in other work, e.g.: (a) Rivetti, F.; Romano, U. *J. Organomet. Chem.* 1978, 154, 323-326. (b) Rivetti, F.; Romano, U. *J. Organomet. Chem.* 1979, 174, 221-6. (c) Burk, P. L.; Van Engen, P.; Campo, K. S. *Organometallics* 1984, 3, 493-5. (d) Fendon, P. M.; Steinwald, P. J. *J. Org. Chem.* 1974, 39, 701-704. (e) Rivetti, F.; Romano, U. *Chim. Ind. (Milan)* 1980, 62, 7-12.

(15) For leading references see "Principles and Applications of Organotransition Metal Chemistry"; Collman, Hegedus, Eds.; University Science Books: Mill Valley, CA, 1980; pp 260-288. This reported insertion reaction shows the general coordination followed by insertion behavior evident in reactions of CO with M-C bonds.

(16) A communication by W. M. Reese and J. D. Atwood (*Organometallics* 1985, 4, 402-4) reported generation of charged species on addition of CO to $\text{ROIr}(\text{CO})(\text{PPh}_3)_2$ at low temperature. It was not yet possible to determine if these ions are on the reaction path to the ultimate $\text{RO}_2\text{C}(\text{CO})_2(\text{PPh}_3)_2$ products.

(Chloromethyl)lithium: Efficient Generation and Capture by Boronic Esters and a Simple Preparation of Diisopropyl (Chloromethyl)boronate

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Summary: (Chloromethyl)lithium is efficiently generated and captured at -78 °C by adding *n*-butyllithium to a

mixture of iodochloromethane and a boronic ester in tetrahydrofuran, resulting in conversion of boronic esters, $RB(OR')_2$, to their homologues, $RCH_2B(OR')_2$, with retention of the configuration of the R group. With triisopropyl borate in place of the boronic ester, a high yield of diisopropyl (chloromethyl)boronate is obtained.

(Chloromethyl)lithium generated in the presence of a boronic ester provides a simple and efficient means of inserting a methylene group into the carbon-boron bond. This new operation is a useful adjunct to our highly efficient directed chiral synthesis with boronic esters.¹⁻³ Only indirect methylene insertions involving reduction of an (α -haloalkyl)boronic ester⁴ or desilylation of an α -trimethylsilyl boronic ester⁵ have been reported previously. (Chloromethyl)lithium with triisopropyl borate also provides the first satisfactory route to (halomethyl)boronic esters. These are highly useful precursors to substrates for the chiral synthesis,⁶ but previous syntheses have been laborious,⁷⁻¹⁰ and the (halomethyl)metal compounds that should solve the problem have been elusive. The direct insertion of (halomethyl)lithium performed at -110°C into cyclic boronic esters has recently been reported to yield 53-71% of the ring-expanded products,¹¹ but our own attempts to carry out similar procedures on boric or boronic esters have been unsuccessful,¹² presumably because of the lability of (chloromethyl)lithium^{13,14} or analogous Grignard reagents.¹⁵ We now report a surprisingly simple solution to these problems.

Cooke has recently shown that lithium/iodine exchange between butyllithium and alkyl iodides is faster than competing attack of butyllithium on carboxylic esters, though not on unhindered ketones.¹⁶ The reactivity of boronic esters toward lithium reagents appears to lie between that of esters and ketones,¹⁷ and butyllithium probably attacks iodochloromethane faster than ordinary alkyl iodides. Thus, it is reasonable that butyllithium might convert iodochloromethane to (chloromethyl)lithium in the presence of a boronic ester.

The results, summarized in Table I, have exceeded expectation. Addition of *n*-butyllithium to a mixture of a

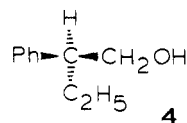
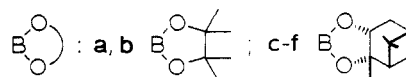
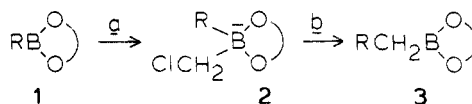
Table I. Homologation of $RB(O_2Z)$ (1) to $RCH_2B(O_2Z)$ (3), Where (O_2Z) Is a Pinacol ($O_2C_2Me_4$) or Pinanediol ($O_2C_{10}H_{16}$) Group

| substr | R | Z | anal. | yield, ^a % | |
|--------|--------------------------------------|---------------------------------|-------|-----------------------|-------|
| | | | | 3 | 1 |
| 1a | CH ₃ | C ₂ Me ₄ | GC | (93.4) | (6.6) |
| 1b | CH ₂ =CH | C ₂ Me ₄ | GC | 90.4 | 9.6 |
| 1c | (CH ₃) ₂ CH | C ₁₀ H ₁₆ | GC | 94 | 6 |
| 1d | C ₆ H ₅ | C ₁₀ H ₁₆ | NMR | 96 | 4 |
| 1e | PhCH ₂ OCH ₂ | C ₁₀ H ₁₆ | NMR | 90 | 10 |
| 1f | C ₂ H ₅ CH(Ph) | C ₁₀ H ₁₆ | NMR | 95 | |

^aFrom weight and composition of product after bulb to bulb distillation, except that the 3a/1a figures represent only a ratio because of nonseparation from BuI.

boronic ester (1) and iodochloromethane in tetrahydrofuran (THF) at -78°C followed by warming to 25°C efficiently yields the homologous boronic ester 3, together with 1-iodobutane and a small amount of unconverted 1. The reaction is postulated to proceed via the usual type of borate complex (2).¹⁸ The facility of the rearrangement step is demonstrated by the high yields where R = CH₃ (1a) or R = PhCH₂OCH₂ (1e), groups which previously gave poor results in uncatalyzed homologations with (dichloromethyl)lithium.² The high yield where R = CH=CH₂ (1b) implies that the reported mediocre yields in the useful Wuts synthesis of allylic boronic esters,¹⁹ which involves rearrangement of similar (chloromethyl)borates (2), can probably be greatly improved.

This homologation is potentially useful in the synthesis of compounds having a methylene group between two chiral centers. Retention of the configuration of R is required by the mechanism¹⁸ and proved for related reactions.^{1,2} To demonstrate, recrystallized (*S*)-pinanediol (α S)-(α -chlorobenzyl)boronate²⁰ with ethylmagnesium bromide yielded the (1-phenylpropyl)boronate (1f). Homologation of 1f with (chloromethyl)lithium yielded 3f, which was oxidized to (+)-(2*S*)-2-phenyl-1-butanol (4). 4 was purified by chromatography on silica and bulb to bulb distillation, $[\alpha]_D^{25} +31.0^\circ$ (*c* 3.6, ether), purity $\geq 99\%$ by GC and 90-MHz NMR analyses. The estimated rotation for optically pure 4 in ether is $+30.9^\circ$ based on the observed $[\alpha]_D^{25} +30.0^\circ$ (*c* 3.5, ether) of a sample which had $[\alpha]_D +18.9^\circ$ (neat)²¹ and an evidently purer sample, $[\alpha]_D +19.45^\circ$ (neat).²²



a, R = CH₃; b, R = CH₂=CH; c, R = (CH₃)₂CH; d, R = Ph; e, R = PhCH₂OCH₂; f, R = PhCH(Et); see 4 for absolute configuration.

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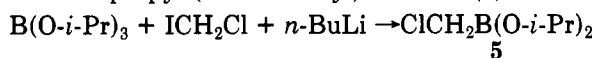
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Generation of (chloromethyl)lithium in the presence of triisopropyl borate followed by acidification efficiently yields diisopropyl (chloromethyl)boronate (5).



In a typical procedure, 5 mmol of boronic ester (1) and 5.4 mmol of iodochloromethane in 20 mL of rigorously dried THF was cooled to -78°C and stirred under argon during the dropwise addition of 5.3 mmol of 1.6 M *n*-butyllithium in hexane. (If the addition was too rapid, the solution turned yellow.) The mixture was kept overnight at $20\text{--}25^\circ\text{C}$, concentrated under vacuum, and treated with petroleum ether and concentrated aqueous ammonium chloride. The organic phase was dried over magnesium sulfate and the product 3 distilled bulb to bulb under vacuum. Products were characterized by 90- or 200-MHz ^1H NMR, and some were also analyzed by gas chromatography (Table I).^{23,24}

To prepare diisopropyl (chloromethyl)boronate (5), 30 mL (48 mmol) of 1.6 M *n*-butyllithium in hexane was added dropwise down the side of the flask to a solution of 3.8 mL (52 mmol) of iodochloromethane and 12 mL (51 mmol) of triisopropyl borate in 60 mL of THF stirred under argon in a -78°C bath. The mixture was allowed to warm to 10°C and then acidified with ethereal hydrogen chloride²⁵ to the end point with methyl orange (added as crystals). Rapid simple distillation under vacuum followed by fractionation through a short Vigreux column yielded 7.2 g (84%) of 5: bp $65\text{--}70^\circ\text{C}$ (20 torr); NMR same as reported.¹⁰

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(23) Most of these boronic esters have been reported previously: 1b,¹⁷ 1c,¹⁶ 1d,²¹ 3b and 3c,⁵ 1e and 3d.²⁴ A report of 1a gave no data [Ulmschneider, D.; Goubeau, J. *Chem. Ber.* **1957**, *90*, 2733-2738]; we found the following data: bp $119\text{--}121^\circ\text{C}$, 90-MHz NMR (CDCl_3) δ 0.22 (s), 1.24 (s). Anal. Calcd for $\text{C}_7\text{H}_{15}\text{BO}_2$: C, 59.21; H, 10.65; B, 7.61. Found: C, 59.45; H, 10.35; B, 7.60. Only ^{17}O data have been reported for 3a [Wrackmeyer, B.; Köster, R. *Chem. Ber.* **1982**, *115*, 2022-2034]; ^1H NMR (CDCl_3) δ 0.9 (m), 1.25 (s). New compounds include 3e: 200-MHz NMR δ 4.53 (s, 2, PhCH_2), 3.645 (t, 2, $\text{OCH}_2\text{CH}_2\text{B}$), 1.27 (t, partially obscured, $\text{OCH}_2\text{CH}_2\text{B}$), other Ph and pinanediol peaks as expected. Anal. Calcd for $\text{C}_{13}\text{H}_{27}\text{BO}_2$: C, 72.62; H, 8.66; B, 3.44. Found: C, 72.72; H, 8.71; B, 3.42. For 1f: bp $135\text{--}137^\circ\text{C}$. Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{BO}_2$: C, 76.52; H, 9.13; B, 3.62. Found: C, 76.54; H, 8.84; B, 4.02.

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react with $\text{Co}_2(\text{CO})_8$ to form, in high yield, the novel "thiocubane" clusters $\text{M}_2\text{Co}_2(\mu_3\text{-S})_4(\text{S}_2\text{CNET}_2)_2(\text{CO})_2\text{-}(\text{CH}_3\text{CN})_2$ ($\text{M} = \text{Mo, W}$). X-ray crystallography shows these clusters to contain a fully metal-metal bonded tetrahedral core as would be predicted from the 60-electron count.

Homometallic "thiocubane" clusters containing an $\text{M}_4\text{-}(\mu_3\text{-S})_4$ core have been known for some time.¹ Current interest in the Fe-Mo cofactor of nitrogenase,² and in the active site structure of group 8-10¹⁸ "promoted", MoS_2 -based hydrotreating catalysts,³ has led to preparation of several heterometallic thiocubanes.^{1,2,4-8} In the earlier studies,² the synthetic approach was "spontaneous assembly". However, advances in homometallic transition-metal sulfide chemistry have led to smaller clusters which are fragments of the thiocubane unit. These fragments are potential building blocks for heteronuclear thiocubane clusters, and recently this potential appears to have been realized in the use of $\text{Cp}_2\text{M}_2\text{S}_4$ and related compounds to form clusters with $\text{M}_2\text{M}'_2(\mu_3\text{-S})_4$ cores.⁵⁻⁷ In this communication we report the use of $\text{M}_2\text{S}_4(\text{S}_2\text{CNET}_2)_2$ to form a thiocubane of the type $\text{M}_2\text{Co}_2(\mu_3\text{-S})_4\text{-}(\text{S}_2\text{CNET}_2)_2(\text{CO})_2\text{L}_2$, where L is a solvent or other Lewis base molecule and $\text{M} = \text{Mo}$ or W . A virtue of this approach is the ready availability of a wide variety of $\text{M}_2\text{S}_4^{2+}$ core compounds having sulfur or nitrogen ligands replacing the dithiocarbamate ligands.⁹ This flexibility provides structural and electronic variation which is not present in the cyclopentadienyl-based systems.

When a solution of $\text{Co}_2(\text{CO})_8$ in THF is mixed with an equimolar amount of $\text{Mo}_2\text{S}_4(\text{S}_2\text{CNET}_2)_2$ under an inert atmosphere, rapid evolution of CO is observed, $\text{Mo}_2\text{S}_4\text{-}(\text{S}_2\text{CNET}_2)_2$ dissolves, and the solution turns a dark green-black color. Addition of hexane leads to precipitation of a dark green-black complex, 1. Characteristic infrared bands due to $\text{Mo}=\text{S}$ (545 cm^{-1}) and $\text{Mo}_2(\mu\text{-S})_2$ (465 cm^{-1}) vibrations are replaced by a broad, medium strength band at 515 cm^{-1} and several slightly weaker bands at 393, 365, and 334 cm^{-1} . A strong, broad terminal CO band is apparent at 1980 cm^{-1} , and a number of characteristic Et_2NCS_2 bands are retained. When 1 is dissolved under N_2 in a minimum of acetonitrile, filtered, and allowed to stand, large black crystals of $\text{Mo}_2\text{Co}_2(\mu_3\text{-S})_4(\text{S}_2\text{CNET}_2)_2\text{-}(\text{CO})_2(\text{CH}_3\text{CN})_2$, 2, are formed.¹⁰ The cluster 2 can also be prepared in microcrystalline form by direct reaction of $\text{Co}_2(\text{CO})_8$ with $\text{Mo}_2\text{S}_4(\text{S}_2\text{CNET}_2)_2$ in CH_3CN . The analo-

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Construction of Heterometallic "Thiocubanes" from $\text{M}_2\text{S}_2(\mu\text{-S})_2$ Core Complexes: Synthesis of $\text{Co}_2\text{M}_2\text{S}_4(\text{S}_2\text{CNET}_2)_2(\text{CH}_3\text{CN})_2(\text{CO})_2$ ($\text{M} = \text{Mo, W}$) and Structure of the $\text{Co}_2\text{Mo}_2(\mu_3\text{-S})_4$ Cluster

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Summary: Molybdenum and tungsten diethyldithiocarbamate complexes containing the $\text{M}_2\text{S}_2(\mu\text{-S})_2$ core