one of the exocyclic oxygens and NH_3 is normal (2.71 (3) and 2.62 (3) Å between O(4)/O(41) and NH(1)/NH(11) in **3**, 2.71 (2) Å between O(2) and NH(1) in **4**). The steric crowding around Pt causes deviations from strict octahedral geometry about the Pt such as to relieve the repulsion between the O atoms and the Cl ligands, e.g., Cl(3)–Pt–Cl(2) 172.3 (1)°, N(3)–Pt–Cl(2) 95.1 (3)°, Cl(2)–Pt–NH(2) 85.7 (4)° in **4**.

Unlike the ^1H NMR spectra of ammine complexes of Pt(II), which only exhibit ^{195}Pt–^1H coupling, the NH_3 resonances of **2–4** show both ^{14}N–^1H (J = 53 Hz) and ^{195}Pt–^1H coupling ($J \simeq 50$ Hz), leading to a characteristic seven-line pattern in the 5–7 ppm region (Figure 3).[18]

In summary, it has been shown that in aqueous solution Cl_2 not only oxidizes Pt(II) in *cis*-$(NH_3)_2$Pt(1-MeU)Cl to the corresponding Pt(IV) complex but at the same time causes substitution of H(5) of the 1-MeU ligand by Cl and subsequently addition of HOCl to the 5.6 double bond of the 5-chloro-1-methyluracil ligand. The isolated complexes are the first examples of pyrimidine-2,4-dione nucleobases containing a hexacoordinated metal bound through N(3).

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Supplementary Material Available: Additional crystal structure data, atomic positional parameters for **3** and **4**, and ^1H NMR data of **2–4** (12 pages). Ordering information is given on any current masthead page.

(18) The asymmetry of the seven-line pattern of the NH_3 resonances most likely arises from the involvement of one of the six ammine protons in hydrogen bonding, rather than from the geometric inequivalence of the two NH_3 groups, since most *cis*-$(NH_3)_2$PtXY complexes show only one set of NH_3 resonances. Hydrogen bonding is expected to shift the resonance of the proton involved to lower field. In *cis*-$(NH_3)_2PtCl_4$ the seven-line pattern is completely regular, 1:4:2:4:2:4:1.

Exceptionally Facile Reduction of Acyclic and Alicyclic Carboxylic Acids to Aldehydes by Thexylchloroborane–Dimethyl Sulfide

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The discovery of an exceptionally facile reduction of acyclic and alicyclic carboxylic acids to alcohols by borane–tetrahedrofuran revolutionized the reduction of this ordinarily very resistant group for synthetic work.[4] We wish now to report an equally facile reduction of such carboxylic acids to aldehydes by thexylchloroborane–dimethyl sulfide.[5]

Numerous reagents have been proposed to achieve this objective.[6] Unfortunately, the ideal reagent has not yet been described.

Table I. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with Thexylchloroborane–Dimethyl Sulfide in Methylene Chloride at Room Temperature[a]

acid	yield of aldehyde, % by analysis with (2,4-dinitrophenyl)-hydrazine	yield of aldehyde, % by isolation using sodium bisulfite adduct[b]
hexanoic	99	83[c]
decanoic	97	89
stearic	98	92
pivalic	98[d]	71[c,d]
cyclohexanecarboxylic	91	80
cyclopentanecarboxylic	89	82
1-adamantanecarboxylic	99	88
diphenylacetic	91	83
1,10-decanedicarboxylic	97	93
6-bromohexanoic	98	86
adipic acid monoethyl ester	93–100[e]	81
benzoic	59	47
p-methoxybenzoic	51	46
p-nitrobenzoic	86	71
m-cyanobenzoic	83	67

[a] Reacted with 10% excess reagent (2.2 equiv for monocarboxylic and 4.4 equiv for dicarboxylic acid) for 15 min with aliphatic and for 24 h with aromatic carboxylic acids, both at room temperature after the hydrogen evolution at 0 °C. [b] Yields are based on the analytically pure aldehydes isolated after evaporation of solvent, following treatment of the adduct with formaldehyde. [c] Yields on distillation of the regenerated product. [d] Reacted for 3 h; 62% for 15 min. [e] A mixture of the (2,4-dinitrophenyl)hydrazones of 5-carboethoxypentanal and 5-carboxypentanal.

At one time the reaction of thexylborane with carboxylic acids appeared promising.[6b] However, the reaction was slow, requiring refluxing in THF for 36 h. Under these conditions, many other groups undergo reduction.

In the course of exploring the reducing action of thexylchloroborane,[6] we observed that acyclic and alicyclic carboxylic acids are reduced to aldehydes in high yields in a matter of minutes at 25 °C. This intrigued us. A simple reduction of carboxylic acids to aldehydes has long escaped us. We have utilized the reduction of acid chlorides by lithium tri-*tert*-butoxyaluminum hydride[7] (LTBA) and the reduction of nitriles[8] and dimethylamides[9] by "lithium diethoxyaluminum hydride", as well as the reduction of acylaziridines by lithium aluminum hydride.[10] Finally, the reduction of carboxylic acid by thexylborane, referred to above, had been explored.[6b] But a really clean reduction had escaped us.

The reagent, thexylchloroborane–dimethyl sulfide, is readily synthesized by treating thexylborane–dimethyl sulfide with 1 equiv of hydrogen chloride[5a] or by hydroborating 2,3-dimethyl-2-butene with monochloroborane–dimethyl sulfide in methylene chloride.[5c] We discovered that this new reaction, based on this reagent, provides an apparently ideal procedure. It reduces aliphatic carboxylic acids to aldehydes in approximately 15 min at room temperature in yields of 93–99%. Alicyclic derivatives, such as cyclohexanecarboxylic acid, cyclopentanecarboxylic acid, and

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1-adamantanecarboxylic acid, work equally well.

Derivatives are readily accommodated. Thus, diphenylacetic acid yields the corresponding aldehyde in a yield of 91%. Similarly, 6-bromohexanoic acid is readily converted to the aldehyde in a yield of 98%. Dicarboxylic acids, such as 1,10-decanedicarboxylic acid, provide the corresponding aldehydes in a yield of 97%. Finally, it is possible to reduce the half-ester of adipic acid to the corresponding ester aldehyde almost quantitatively.

Just as in the reduction of carboxylic acids with borane–tetrahydrofuran, the reduction of aromatic acids with thexylchloroborane is much more sluggish. The reaction requires 24 h and the yields are significantly lower and vary with the substituent. For example, both benzoic and *p*-anisic acids give yields of 51–59%, whereas, *p*-cyano- and *p*-nitrobenzoic acids give substantially better yields (83–86%).

Fortunately, the reduction of acid chlorides by LTBA is especially favorable for aromatic derivatives. Consequently, the two procedures complement each other, with the thexylchloroborane being ideal for aliphatic derivatives and the LTBA method being ideal for aromatic derivatives.

The remarkable difference in rates in the reduction by thexylchloroborane of aliphatic carboxylic acids, on the one hand, and aromatic carboxylic acids, on the other, suggests the possibility of achieving the selective reduction of a carboxylic acid group attached to an aliphatic or alicyclic moiety in the presence of a carboxylic acid group attached to an aromatic moiety. This possibility was tested in the following manner. A mixture of equimolar amounts of cyclohexanecarboxylic acid and benzoic acid was treated with 3 mmol equiv of thexylchloroborane (2 for hydrogen evolution and 1 for reduction). After 1-h reaction at room temperature, GC analysis of the product revealed a 93% yield of cyclohexanecarboxaldehyde, with only traces of benzaldehyde.

We explored several methods for the isolation of aldehyde products. We encountered no significant problems with such isolation. However, the well-known bisulfite procedure[11] appeared to be broadly applicable. Consequently, this procedure was adopted for our exploration of the scope of the reaction.

The following procedure for the reduction of 6-bromohexanoic acid is representative. An oven-dried, 100-mL flask, fitted with a side arm and a bent adapter connected to a mercury bubbler, was flushed with nitrogen and charged with 10.53 g (54 mmol) of 6-bromohexanoic acid and 16 mL of methylene chloride. The flask was immersed in an ice-water bath and a precooled solution of thexylchloroborane–dimethyl sulfide (39.6 mL, 3 M, 118.8 mmol, 10% excess) in methylene chloride was added dropwise with vigorous stirring. After the complete evolution of the hydrogen, the ice-water bath was removed and the reaction mixture was stirred for 15 min at room temperature. Analysis of an aliquot with 2,4-dinitrophenylhydrazine indicated a yield of 98%: mp of the hydrazone, 92–93 °C. Anal. Calcd: C, 40.12; H, 4.21; N, 15.60; Br, 22.25. Found: C, 39.97; H, 4.23; N, 15.59; Br, 22.07.

The rest of the reaction mixture (50 mmol) was transferred via a double-ended needle to the flask containing 50 mL of cold water in an ice-water bath and then hydrolyzed with vigorous stirring for 1 h at room temperature. The mixture was saturated with sodium chloride and the organic layer was separated.

After neutralization with a small amount of sodium bicarbonate, the organic layer was poured into 75 mL of a saturated aqueous sodium bisulfite solution and 70 mL of tetrahydrofuran was added. The mixture was stirred for 1 h. At this time the crystalline bisulfite adduct of 6-bromohexanal was apparent. The solution was cooled in an ice-water bath to ensure complete crystallization of the adduct. The adduct was then collected by filtration and washed with 3 × 25 mL of pentane and dried. The adduct was placed in 50 mL of a saturated aqueous magnesium sulfate solution and then 50 mL of pentane and 8 mL of a 37% formaldehyde solution were added. The mixture was stirred for 1 h. The pentane layer was separated and dried with anhydrous magnesium sulfate. Evaporation of all volatile materials gave an 86% yield of the almost pure product.

Distillation of the crude product gave 6.8 g (76%) of pure 6-bromohexanal: bp 106–107 °C (14 mm); n^{20}_D 1.4788. Anal. Calcd: C, 40.24; H, 6.19; Br, 44.63. Found: C, 40.12; H, 5.89; Br, 44.35.

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A Novel Olefin Bridged Dinuclear Arylpalladium Compound. X-ray Crystal Structure of $[NMe_2CH_2C_6H_4Pd\text{-}\mu\text{-}\{C(CF_3)=C(CF_3)C(CF_3)=C(CF_3)\}PdCH(SiMe_3)C_6H_4NMe_2]$

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Directed C–C bond formation between different organo groups at a neutral metal center has become an important route in organic synthesis for the construction of new molecules.[1] It is now well established that cyclopalladated molecules, especially those with nitrogen as the donor atom, are reactive intermediates in this purpose.[2] Recently we showed that alkynes may readily insert into the Pd–C bonds of cyclopalladated tertiary amines.[3] In the course of our studies to shed some light on the selectivity of these new C–C bond formations we investigated the reactivity of [Pd{CH(R)$C_6H_4NMe_2$-2}R'] (**a**, R' = 2-(dimethylamino)methylphenyl (dmba); **b**, R' = 8-methylquinoline (8-mq); Scheme I) with R = H (**1**) or $SiMe_3$ (**2**) toward $CF_3C{\equiv}CCF_3$. Whereas **1** did not lead to any identifiable organometallic product,[3] we now report that the novel trimethylsilyl derivative **2** reacts readily to give selective asymmetric oxidative coupling of the cyclometallated organo groups and formation of a novel unsymmetrical dinuclear Pd species containing a bridging dimer of the alkyne.

Reaction of α-lithiated 2-(dimethylamino)-α-(trimethylsilyl)-methylbenzene with the chloro-bridged dimers $(PdClR')_2$ afforded in good yields the bicyclic compounds **2** (Scheme I). A crystal structure of analogous Pd[CH($SiMe_3$)$C_6H_4NMe_2$-2][C_6H_4CH(Me)NMe_2-2-(S)] (**2c**), which exists as one diastereomeric pair, unambigously proved the cis geometry of this class of compounds.[4]

Compounds **2a** and **2b** reacted with excess of $F_3CC{\equiv}CCF_3$ to give compounds **3a** (ca. 20%) and **3b** (ca. 60%), respectively, together with 1 equiv of the oxidative coupling product (e.g., **4b**; FD mass spectra, *m/e* 348 found (calcd *m/e* 348)). The elemental

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