cell parameters $a = 11.871$ (9) Å, $b = 9.052$ (7) Å, $c = 14.299$ (1) Å, $\beta = 115.19$ (4)°, and $D_{\mathrm{calcd}} = 1.31$ g cm^{-3} for $Z = 2$. Least-squares refinement based on 1310 observed reflections with intensities $I \geq 3\sigma(I)$ in the range of $2.00° \leq 2\theta \leq 50.0°$ converged at $R = 0.0789$ ($R_w = 0.0949$). Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were placed in idealized positions with fixed isotropic temperature factors.

The title compound bears a striking resemblance to $\mathrm{Al_2N_2}$ condensation products obtained from high-temperature $\mathrm{R_2N{-}H/AlR_3}$ reactions. Fundamental studies of such reactions of aluminum alkyls with simple monodentate amines were reported by Smith.[25–33] These reactions, referred to as intermolecular condensations, initially produce simple $\mathrm{R_2N{-}H{:}AlR_3}$ adducts at room temperature. Increase in reaction temperature, however, results in cleavage of N–H and Al–R bonds, the evolution of alkane, and the subsequent formation of $\mathrm{Al_2N_2}$ fragments in the reaction products.

As can be seen from the X-ray crystal structure of $\mathrm{[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2}$ (Figure 1), the title compound resides on a crystallographic center of symmetry with a planar $\mathrm{Al_2N_2}$ four-membered ring occupying the central cavity of the macrocycle. The $\mathrm{Al_2N_2}$ ring is asymmetric with independent Al–N distances of 1.954 (6) and 1.945 (6) Å for Al(1)–N(2) and Al(1)–N(2a), respectively. The Al(1)···Al(1a) separation of 2.768 (3) Å does not indicate significant metal–metal interaction. Characteristic of compounds containing $\mathrm{Al_2N_2}$ four-membered rings,[29,31,32] the N–Al–N and Al–N–Al bond angles approach 90° (89.6 (3)° and 90.4 (4)° for N(2)–Al(1)–N(2a) and Al(1)–N(2a)–Al(1a), respectively). The bond angle of the ethylaluminum fragment, Al(1)–C(6)–C(7), is 117.8 (7)°. The independent Al–Cl distances are 2.172 (3) and 2.163 (4) Å (for Al(2)–Cl(1) and Al(2)–Cl(2), respectively) while the Cl(1)–Al(2)–Cl(2) bond angle is 117.8 (8)°.

The title compound contains two $\mathrm{(C_2H_5)AlCl_2}$ units. Therein lies the most striking feature of $\mathrm{[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2}$: the absence of diethylaluminum chloride moieties. The presence of the $\mathrm{(C_2H_5)AlCl_2}$ units may possibly be accounted for by the disproportionation of $\mathrm{[(C_2H_5)_2AlCl]_2}$ to give $\mathrm{(C_2H_5)AlCl_2}$ and $\mathrm{(C_2H_5)_3Al}$. Indeed, dialkylaluminum halides have been shown to disproportionate in the presence of base to give alkylaluminum dihalides and trialkylaluminum.[34] Thus, it is quite reasonable that the disproportionation products resulted from a transient mixed alkyl–halo isomer (Figure 2) of the diethylaluminum chloride dimer. Transient existence of such a dimeric species for diethylaluminum chloride was initially suggested by Ziegler nearly 30 years ago.[35] Bridge cleavage of such a dimer would provide both $\mathrm{(C_2H_5)AlCl_2}$ and $\mathrm{(C_2H_5)_3Al}$ (Figure 2). The title compound could thus be obtained by the stronger Lewis acid, $\mathrm{(C_2H_5)AlCl_2}$, preferentially forming adducts with two nitrogen atoms of the macrocycle. The remaining $\mathrm{(C_2H_5)_3Al}$ species in solution is available to react, upon heating, with the N–H units along the macrocyclic cavity (resulting in the $\mathrm{Al_2N_2}$ fragment). The overall reaction is given in eq 1.

$$\mathrm{2AlEt_3 + 2EtAlCl_2 + C_{10}H_{24}N_4 \rightarrow [AlEt]_2[C_{10}H_{20}N_4][AlEtCl_2]_2 + 4Et{-}H} \quad (1)$$

The reaction of $\mathrm{AlR_3}$ with macrocyclic amines possessing N–H units has been previously noted in this laboratory.[18–21] Characteristically, the products of such reactions possess $\mathrm{Al_2N_2}$ fragments along the interior of the macrocyclic cavity that are isostructural with that of the title compound. Additionally, in all such reactions alkane is released. The isolation of the title compound has stimulated our interest in Al–N cage products, and studies are currently underway with regard to other organoaluminum species and multidentate amines.

Acknowledgment. We are grateful to the National Science Foundation for support of this work to G.H.R. (RII-8520554).

Registry No. $\mathrm{[Al(C_2H_5)]_2[C_{10}H_{20}N_4][Al(C_2H_5)Cl_2]_2}$, 114221-38-4; $\mathrm{C_{10}H_{24}N_4}$, 295-37-4; $\mathrm{(C_2H_5)_2AlCl}$, 96-10-6.

Supplementary Material Available: Tables of crystal data, bond distances and angles, final fractional coordintes, and thermal parameters (8 pages); a listing of observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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Activation of a β-Lactone by Oxidative Addition and the Structure of a Platina(IV)lactone

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Summary: The oxidative addition of the $\mathrm{CH_2{-}O}$ bond of β-propiolactone to $\mathrm{[PtMe_2(NN)]}$ (**1a**, NN = 2,2′-bipyridine; **1b**, NN = 1,10-phenanthroline) gives the corresponding platinalactone derivatives $\mathrm{[PtMe_2\{CH_2CH_2C(O)O\}(NN)]}$ (**2a** and **2b**, respectively). The structure of **2b** has been determined crystallographically [space group *Pbca*; $a = 13.838$ (2), $b = 14.774$ (5), $c = 15.735$ (4) Å; $Z = 8$; $R = 0.035$ for 836 reflections]. Oxidative addition follows second-order kinetics, and the rate does not correlate with solvent polarity though the reaction is faster in hydroxylic solvents.

Metallalactones are probable intermediates in many transition-metal-catalyzed reactions involving formation of lactones or their derivatives and in the activation of lactones in organic synthesis,[2] but such complexes have

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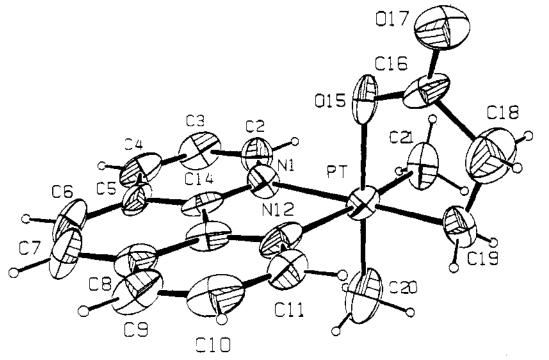


Figure 1. A view of the structure of **2b**. Selected parameters [bond distances (Å) and bond angles (deg)] for the platinalactone ring: Pt–O(15), 2.099 (11); O(15)–C(16), 1.26 (2); C(16)–O(17), 1.26 (2); C(16)–C(18), 1.56 (3); C(18)–C(19), 1.47 (3); Pt–C(19), 2.006 (17); Pt–O(15)–C(16), 111.9 (9); O(15)–C(16)–C(18), 118 (2); C(16)–C(18)–C(19), 113 (2); C(18)–C(19)–Pt, 109 (1); O(15)–Pt–C(19), 84.9 (6).

rarely been isolated[3] and we know of no case where they have been isolated by oxidative addition of lactones. Indeed, activation of the C–O bond of saturated esters is normally difficult and is largely limited to methyl tosylate and similar derivatives with good leaving groups.[4] This paper reports the easy oxidative addition of β-propiolactone to the complexes [$PtMe_2$(NN)] (**1a**, NN = 2,2′-bipyridine; **1b**, NN = 1,10-phenanthroline) to give the products [$PtMe_2\{CH_2CH_2C(O)O\}$(NN)] (**2a** and **2b**, respectively).

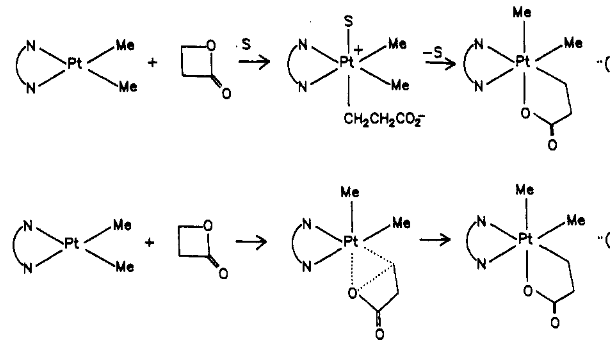
The reaction occurred at room temperature, and the colorless products *2* were characterized by elemental analysis, by ^1H and ^{13}C NMR spectroscopy,[5] and, for **2b**, by X-ray structure analysis.[6] The structure of **2b** is shown in Figure 1.

The oxidative addition reactions follow good second-order kinetics, first order in both complex **1** and propiolactone, in several solvents (Table I), and there was no evidence for free radical intermediates.[7a] The two most probable mechanisms consistent with second-order kinetics are shown in eq 1 and 2.

Table I

solv	E_T[a]	[$PtPh_2$(bpy)][b] k_2 (40 °C), L mol^{-1} s^{-1}	[$PtMe_2$(bpy)][c] k_2 (25 °C), L mol^{-1} s^{-1}
toluene	33.9		2.8×10^{-3}
benzene	34.5	1.1×10^{-1}	
ethyl acetate	38.1	1.9×10^{-1}	2.4×10^{-3}
dichloromethane[d]	41.1	3.5×10^{-1}	1.3×10^{-2}
acetone	42.2	6.75×10^{-1}	2.2×10^{-3}
acetonitrile	46.0		8.5×10^{-3}
nitromethane	46.3	1.5	
tert-butyl alcohol[d]	43.9		1.1×10^{-1}
isopropyl alcohol[d]	48.6		1.0×10^{-1}
methanol[d]	55.5		8.7×10^{-2}

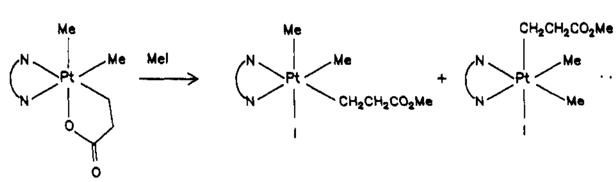
[a] Reichardt parameter of solvent polarity. [b] Reaction with MeI.[7b] [c] Reaction with β-propiolactone. For comparison, the corresponding rate constants for **1b** at 27 °C were 5.4×10^{-4} in benzene, 1.3×10^{-3} in acetone, and 1.5×10^{-1} L mol^{-1} s^{-1} in methanol. [d] Complex 1 reacts with these solvents, but these reactions were negligibly slow under the reaction conditions used. The product in each case was 2 only, so long as solutions were prepared immediately before each kinetic run.



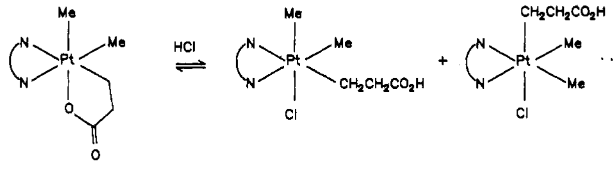
(1)

(2)

Equation 1 is an S_N2 mechanism leading to a zwitterionic intermediate and is analogous to the mechanism of oxidative addition of primary alkyl halides to complex 1,[7] while eq 2 is a concerted mechanism. The data in Table I show that the rate of oxidative addition of propiolactone is much faster in hydroxylic solvents, probably due to enhanced hydrogen bonding to a more polar carboxylate group in the transition state.[7,8] The activation parameters were E_a = 49 (±4), 46 (±2), and 34 (±2) kJ mol^{-1} and $\Delta S^{\ddagger}$ = −129, −142, and −151 J K^{-1} mol^{-1} in solvents toluene, acetone, and methanol, respectively, and the large negative values of $\Delta S^{\ddagger}$ are similar to those found for oxidative addition of alkyl halides by the S_N2 mechanism.[1,7] However, whereas the rates of oxidative addition of alkyl halides to 1 and related compounds correlate well with solvent polarity, the rates of reaction with propiolactone show no such correlation (Table I). Thus, while the balance of the



(3)



(4)

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(5) Reaction of [$PtMe_2$(bpy)] (0.1 g) in acetone (10 mL) with β-propiolactone (0.2 mL) at room temperature for 4 h gave **2a** in 93% yield. Anal. Calcd for $C_{15}H_{18}N_2O_2Pt$: C, 39.7; H, 4.0; O, 7.1. Found: C, 39.55; H, 4.25; O, 7.8. Typical spectroscopic data for **2a** (NMR in $CDCl_3$): ^1H, δ 0.17 [s, ^2J(PtH) = 73 Hz, *Me*Pt trans to O], 1.21 [s, ^2J(PtH) = 70 Hz, *Me*Pt trans to N], 2.7–3.7 [m, CH_2CH_2]; ^{13}C, δ −16.4 [CH_3, ^1J(PtC) = 701 Hz, *Me*Pt], −3.7 [CH_3, ^1J(PtC) = 719 Hz, *Me*Pt], 7.37 [CH_2, ^1J(PtC) = 647, PtCH_2], 37.8 [CH_2, ^2J(PtC) = 44 Hz, PtCH_2CH_2], 187 [C, CO_2].

(6) Crystal data for **2b**: $C_{17}H_{18}PtN_2O_2$: fw 477.44; orthorhombic, space group *Pbca*; *a* = 13.838 (2), *b* = 14.774 (5), *c* = 15.735 (4) Å; *V* = 3217 (2) $Å^3$; *Z* = 8, D_{calcd} = 1.97 g cm^{-3}; μ(Mo Kα) = 88.2 cm^{-1}; crystal dimensions 0.19 × 0.52 × 0.54 mm. Data were measured on a CAD-4 diffractometer and corrected for Lorentz, polarization, and absorption effects. Refinement with hydrogen atoms in geometrically idealized positions was by full-matrix least-squares calculations of 200 variable parameters based on 836 unique reflections with $F > 3\sigma(F)$ to give *R* = 0.035 and R_w = 0.044. Details are given in the supplementary material.

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evidence favors the S_N2 mechanism of eq 1, the concerted mechanism of eq 2 cannot be dismissed.[8]

The stereochemistry of **2** at platinum is determined by the requirement that the favorable *fac*-PtR_3 unit (R = alkyl) should be formed while accommodating the platinalactone ring. Reaction of **2b** with methyl iodide leads to formation of $[PtIMe_2(CH_2CH_2CO_2Me)(NN)]$ (eq 3), in which the chelate ring has been broken and the isomers **3a** and **3b** (NN = 1,10-phenanthroline) are present in the ratio 28:72 at equilibrium, though **3a** was formed first as determined by monitoring the reaction by ^1H NMR.[9] Similarly, reaction **2b** with HCl gave a mixture of **4a** and **4b** and this reaction was reversed on addition of base (Proton Sponge).

Acknowledgment. We thank NSERC (Canada) for financial support (to G.F. and R.J.P.).

Supplementary Material Available: Tables of experimental details, positional parameters, molecular dimensions, calculated hydrogen coordinates, thermal parameters, least-squares planes, and torsion angles (11 pages); a listing of observed and calculated structure factors (9 pages). Ordering information is given on any current masthead page.

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(8) The mechanisms could be distinguished unambiguously by determining if reaction occurred with retention or inversion of stereochemistry at carbon. However, β-butyrolactone failed to react with **1**, presumably due to steric hindrance, and so we have been unable to settle this issue.

(9) Reaction of **2b** (0.1 g) in CH_2Cl_2 (50 mL) with MeI (0.25 mL) at room temperature for 16 h gave **3a** in 95% yield. Anal. Calcd for $C_{18}H_{21}IN_2O_2Pt$: C, 34.9; H, 3.4; N, 4.5. Found: C, 34.8; H, 3.4; N, 4.6. NMR data for **3a**: ^1H, δ 1.66 [s, $^1J(PtH) = 71$ Hz, MePt), 2–3 [m, CH_2CH_2], 3.16 [s, *MeO*]; ^{13}C, δ −5.2 [CH_3, $^1J(PtC) = 687$ Hz, MePt], 16.8 [CH_2, $^1J(PtC) = 705$ Hz, CH_2Pt], 34.1 [CH_2, CH_2CH_2Pt], 51.1 [CH_3, *MeO*], 172.9 [C, CO_2].

Book Reviews

Preparative Polar Organometallic Chemistry 1. By L. Brandsma and H. Verkruijsse. Springer-Verlag, Berlin. 1987. xiv + 240 pages. $43.00 (paperback).

Organolithium and Grignard reagents are among the most useful organometallic reagents for synthesis in the organic and organometallic area. The present book, which is a laboratory manual for the preparation and utilization of such reagents formally (but not necessarily actually) derived from sp^2 hydrocarbons (olefins, allenes, cumulenes, arenes, and heteroarenes), is one which synthetic organic and organometallic chemists should have in their personal libraries. It will be of great value to its users because these all are procedures which have been checked in the laboratories of the authors in the State University at Utrecht. In fact, they have been more than simply checked: they have been improved, at times scaled up from millimolar to 0.05–0.1 molar scale and have been made more generally applicable.

Chapter I is a very useful one. It brings a referenced discussion, with many useful practical hints, of strongly basic organometallic reagents (RLi, R_2NLi, MNH_2, RLi·TMEDA, RLi·*t*-BuOK), the solvents and auxiliary bases which facilitate their use, the laboratory equipment used in their preparation and applications, and their safe handling and disposal. Detailed preparative procedures for some of these basic reagents then follow. The second chapter is equally useful. In fact, the authors recommend that it be read before undertaking any of the procedures in which the organometallic reagents are used since it deals broadly with the reactivity of polar organometallic reagents.

All subsequent chapters then bring detailed procedures in which these polar organometallic reagents are used in synthesis, with each chapter devoted to a separate type of reagent: metalated olefinic and allenic hydrocarbons; metalated hetero-substituted unsaturated systems; metalated heteroaromatic compounds; metalated aromatic compounds. A great diversity of reactions (mostly coupling, addition, and insertion processes) as well as polar reagent syntheses is presented. To obtain maximum benefit from this book, the instructions for using the metalation–functionalization and the reaction-type indexes, found at the end, should be consulted.

The original literature relating to the polar reagents which are the subject of this book can be fickle and misleading. Therefore, we have good reason to be grateful to the authors and their co-workers for sharing their considerable experience in this way.

Further volumes dealing with other types of organometallic reagents are planned. They will be as welcome as this one is.

Dietmar Seyferth, *Massachusetts Institute of Technology*

Theoretical Approaches (Volume 68 of Structure and Bonding). Contributions by O. S. Mortensen, D. M. P. Mingos, R. L. Johnston, and O. Kahn. Springer-Verlag, Berlin. 1987. 167 pages. $77.50.

This volume of *Structure and Bonding* contains three rather disparate topics in theoretical chemistry. The first chapter (28 pages), by O. S. Mortensen, develops an alternative approach to point group symmetry. Eigenfunctions are found to noncommuting operators for the particular symmetry group. This noncommuting generator approach is then used for problems with half-integer spin and time-reversal symmetry. Despite the plea in the Introduction, I suspect that this approach will remain rather esoteric for most people who need and use group theory.

The second chapter (58 pages), by Mingos and Johnston, covers models that have been used to develop qualitative ideas about the bonding in clusters. This includes the styx model, the polyhedral skeletal electron pair theory, the isolobal analogy, etc. Nearly half of the chapter is devoted to Tensor Surface Harmonic theory which was developed by A. J. Stone in 1980 and popularized by Mingos in the past couple of years. Although all of the material covered here has been reviewed to varying degrees elsewhere and the coverage of bonding in clusters is certainly not exhaustive, this is a useful addition to the chemical literature. There is great heuristic appeal. All concepts of cluster bonding have been covered and illustrated in enough detail so that workers in the cluster field can rapidly pick up and apply these concepts to their own problems. It should be pointed out that issues relating to reactivity and fluxionality in clusters have not been addressed.

The third chapter (78 pages), by Kahn, is a beautifully written account of the magnetic interactions in transition-metal dimers and trimers. The mechanism of ferromagnetic or antiferromagnetic exchange for many specific examples is covered. The use of orbital symmetry and overlap density to gauge the magnitude of interaction is highlighted. This is a vast field that is skillfully reviewed by the leading theoretician in the area.

In summary, this book is a useful addition to all chemistry libraries. Compared to previous volumes in this series, this one is of exceptionally high quality. It is obvious that the authors have spent much effort to distill the contents into a manageable form. None of the chapters is a simple rehash of literature coverage.

Thomas A. Albright, *University of Houston*