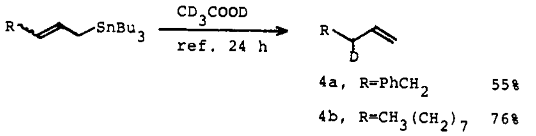
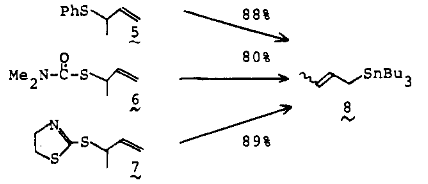
As an additional example, we demonstrated the preparation of deuterated alkenes **4a** and **4b** using acetic-d_3 acid-d.



The usefulness of the present concept for the completely regioselective allylic desulfurization to terminal olefins will be further enhanced if allylic sulfur compounds other than sulfones can be generally transfered to allyltins. This was realized in the following allylic sulfides under similar conditions.[18]



The ready availability of tri-n-butyltin hydride from inexpensive starting materials and the facility of the reaction provide a stimulus for further exploration of its chemistry and the chemistry of allyltins.

A typical procedure[19] is as follows. A mixture of 3-tolylsulfonylnona-1-ene (**1b**, 447 mg, 1.38 mmol), tri-n-butyltin hydride (928 mg, 3.19 mmol), and AIBN (~10 mg) in dry benzene (3 mL) was refluxed under a nitrogen atmosphere for 2 h until the disappearance of the absorption of sulfone at 1320 and 1150 cm^{-1}. After the completion of the reaction, 1-(tri-n-butylstannyl)nona-2-ene (**2b**) was isolated by column chromatography (neutral alumina, eluted with benzene) in 65% yield (443 mg) as a colorless oil. The further purification was carried out by Kugelrohr distillation under reduced pressure: bp 136-142 °C (0.003 mm).

Protolysis of the crude reaction mixture was carried out using concentrated hydrochloric acid (3 mL) or acetic acid (3 mL) at room temperature for several hours. 1-Alkenes **3** were identified by the comparison of GC analysis and spectral data with those of authentic samples.

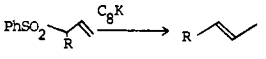
References and Notes

(1) Synthetic Reactions Using Organotin and Sulfur Compounds. 3. For part 2, see ref 5, and for part 1, see Y. Ueno, A. Nakayama, and M. Okawara, *J. Am. Chem. Soc.*, **98**, 7440 (1976).

(2) For leading references, see (a) D. A. Evans and G. C. Andrews, *Acc. Chem. Res.*, **7**, 147 (1974); (b) E. E. van Tamelen, R. A. Holton, R. E. Hopla, and W. E. Konz, *J. Am. Chem. Soc.*, **94**, 8228 (1972); (c) P. A. Grieco and Y. Masaki, *J. Org. Chem.*, **39**, 2135 (1974).

(3) (a) K. Narasaka, M. Hayashi, and T. Mukaiyama, *Chem. Lett.*, 259 (1972); (b) K. Hirai and Y. Kishida, *Tetrahedron Lett.*, 2743 (1972); (c) T. Nakai, H. Shiono, and M. Okawara, *Chem. Lett.*, 249 (1975); (d) T. Hayashi and H. Midorikawa, *Synthesis*, 100 (1975).

(4) Reductive desulfurization of allylic sulfur compounds, especially possessing a terminal double bond, generally gave a mixture of internal and terminal olefins involving double-bond migration; see ref 3 and 2b. In the case of



the following sulfones, complete double-bond migration has been reported: (a) D. Savoia, C. Trombini, and A. Umani-Ronchi, *J. Chem. Soc., Perkin Trans. 1*, 123 (1977). On the other hand, allylic sulfones bearing an internal double bond have been desulfurized without double-bond migration with $LiEtNH_2$; e.g., see (b) B. M. Trost, L. Weber, P. Strege, T. J. Fullerton, and T. J. Dietsch, *J. Am. Chem. Soc.*, **100**, 3426 (1978).

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(6) **1a:** mp 43-44 °C (n-hexane). **1b:** mp 53-54 °C (ether-n-hexane). **1c:** mp 68-69 °C (CCl_4). **1d:** mp 95-96 °C (ether-n-hexane). **1e:** 210-215 °C (0.003 mm) Kugelrohr).

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(8) Tolylsulfonyl moiety was trapped by tin hydride to give tri-n-butyltolylsulfonylstannane (Bu_3SnSO_2Tol). The IR absorptions at 960 and 980 cm^{-1} suggest the sulfinate structure. Cf. W. Kitching, C. N. Fong, and A. J. Smith, *J. Am. Chem. Soc.*, **91**, 767 (1969).

(9) The stereochemistry of allyltins **2** was tentatively determined by its ^{13}C NMR spectrum measured under the conditions of the minimum NOE influence and pulse repetition, 4.5 s. For example, the spectrum of **2b** showed the β carbon to the butyltin group at δ 128.89 and 128.01 (integration, 71:29), and the α carbon at δ 125.97 and 124.56 (integration, 70:30) indicative of its trans:cis ratio being ~70:30. Similar ratios were obtained for **2a, 2c,** and **2d.**

(10) Kugelrohr distillation. **2a:** bp 132-138 °C (0.002 mm). **2b:** bp 136-142 °C (0.003 mm). **2c:** 162-168 °C (0.002 mm). **2d:** bp 186-196 °C (0.002 mm). **2e:** 175-185 °C (0.003 mm).

(11) D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **24**, 1395 (1959).

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(13) γ-Alkylated allylic sulfones such as crotyl tolyl sulfone did not react with tri-n-butyltin hydride. This result is consistent with the observation that organotin hydride generally affords hydrostannylated products toward terminal olefins but not internal olefins: N. P. Neumann and R. Sommer, *Justus Liebigs Ann. Chem.*, **675**, 10 (1964).

(14) For example, a wide variety of electrophiles such as alkyl halides,[15] aldehydes,[16] or pentacarbonylmanganese halide[17] are known to react with allyltins to produce functional alkenes.

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(18) Allylic sulfoxides, however, fail to give allyltin compounds, presumably owing to their facile [2,3]-sigmatropic rearrangement. See ref 2a.

(19) All new compounds obtained here had satisfactory physical and spectral data as well as elemental analyses.

Y. Ueno,* S. Aoki, M. Okawara
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, Nagatsuta
Midoriku, Yokohama 227, Japan

Received April 3, 1979

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^{15}N NMR of *cis*-Diamine-Platinum(II) Complexes in Aqueous Solution[1]

Sir:

The recent interest in the aqueous chemistry of *cis*-diamine-platinum(II) compounds is the result of the discovery by Rosenberg and co-workers[2] in 1969 that *cis*-dichlorodiammineplatinum(II) (DDP) is an antitumor agent. Although DDP and similar compounds have been shown to inhibit DNA synthesis, the exact mode of biological action of these compounds is not known[3] despite a great number of studies of these anticancer agents and their interaction with biomolecules.[4] This has prompted us to explore the potential of ^{15}N magnetic resonance as a probe for determining the biological binding site of these Pt(II) species. Studies have suggested that the uncharged DDP species diffuses through the cell membrane but, once in the cell, dissociates Cl^- to form *cis*-$(NH_3)_2Pt(H_2O)_2{}^{2+}$ which may then attack one or more basic nitrogen sites of the purine or pyrimidine bases in the nucleic acid chain.[5] We have accordingly prepared and recorded ^{15}N spectra for aqueous solutions of *cis*-$(^{15}NH_3)_2Pt(H_2O)_2{}^{2+}$ (**1**), ^{15}N-en$Pt(H_2O)_2{}^{2+}$ (**3**) (^{15}N-en = 100% ^{15}N-labeled ethylenediamine) and for derivatives of **1** and **3** in which one or both H_2O molecules are replaced by 100% ^{15}N-labeled 1-methylimidazole (^{15}N-MeIm). We have found that replacement of H_2O by ^{15}N-MeIm in the Pt(II) complexes produces a large change in both the ^{15}N chemical shift and the ^{195}Pt-^{15}N coupling constant for the $^{15}NH_3$ or ^{15}N-en nitrogens. At the same time, the ^{15}N resonances for both $^{15}N_1$ and $^{15}N_3$ of the ^{15}N-MeIm are shifted from their positions in an aqueous solution of ^{15}N-MeIm and both resonances display satellites due to ^{195}Pt-^{15}N coupling. These results indicate that ^{15}N NMR is a sensitive probe for detecting interactions between *cis*-diamine-platinum(II)$^{2+}$ species and imidazole-ring nitrogen in biological systems (e.g., purine base sites of nucleic acids)

Table I

	1	2	3	4	5	6
^{15}N Shifts[a]						
(a) NH_3 or en	+67.0	+46.4	+45.9	+44.8[b]; +29.7[c]	+28.9	
(b) MeIm						
N_3		+91.9		+93.1	+91.1	+121.0
N_1		−4.7		−4.8	−4.6	−5.4
Couplings[d]						
amine nitrogen						
$^{15}N-H$ (directly bonded)	73.2	72.0	75.4	not observed	not observed	
$^{15}N-^{195}Pt$	388.6	286.5	421.4	411.1[e]; 327[f]	318.9	
imidazole nitrogen						
$^{15}N_3-^{195}Pt$		436.5		not observed	428.6	579.4
$^{15}N_1-^{195}Pt$		26.1		24.7	25.5	32.6
$^{15}N_3-^{15}N$ (amine)		5.4		5.1	5.4	

[a] All shifts are given in parts per million relative to the corresponding uncomplexed amine in dilute aqueous solution at high pH. [b] Singlet. [c] 5.1-Hz doublet. [d] Couplings are in hertz. The signs of the couplings have not been determined. [e] Doublet of singlets. [f] Doublet of 5.1-Hz doublets.

and suggests that other basic binding sites could be identified. The data also show some interesting effects of ligand strength on ^{15}N NMR shifts and $^{195}Pt-^{15}N$ coupling constants in these square-planar Pt(II) complexes.

^{15}N spectral data were taken at 10.16 MHz on a Varian XL-100 spectrometer operated in FT mode. Approximately 0.2 M aqueous solutions of **1**, **3**, and *cis*-(^{15}N-MeIm)$_2$-Pt$(H_2O)_2^{2+}$ (**6**) were separately prepared by the method of Dhara.[6] The pH of such solutions is typically ~2.0. A proton-coupled spectrum of the solution of **1** shows the directly bonded $^{15}N-^{1}H$ coupling (1:3:3:1 quartet) for the equivalent ammine nitrogens and also displays the $^{15}N-^{195}Pt$ coupling (natural ^{195}Pt abundance ≃ 34%, $I = 1/2$) leading to smaller "satellites" of the central quartet. Similarly, a proton-coupled spectrum of **3** displays a 1:2:1 triplet with corresponding ^{195}Pt satellites. The latter spectrum is shown in Figure 1A. Continuous proton decoupling collapses the quartet and triplet structures to inverted singlets indicating a large negative NOE for both **1** and **3**. By adding 2-4 mol of ^{15}N-MeIm per Pt(II) to a solution of **1** or **3**, we obtain solutions which initially contain a mixture of species, but after several days display only the spectral features of *cis*-($^{15}NH_3)_2Pt(^{15}N\text{-MeIm})_2^{2+}$ (**2**) or ^{15}N-enPt(^{15}N-MeIm)$_2^{2+}$ (**5**) and excess ^{15}N-MeIm. The pH of such solutions is typically in the region of 7-9. Reducing the pH to 2.0 with aqueous HNO_3 has no effect on the spectral features of the bound species but converts the unbound excess ^{15}N-MeIm completely to ^{15}N-MeImH$^+$ in which the $^{15}N_1$ and $^{15}N_3$ resonances fortuitously superpose.[7] A proton-decoupled ^{15}N spectrum of such a solution of **5** is shown in Figure 1C. The pH of a solution obtained by adding ~1 mol of ^{15}N-MeIm/mol of **3** is initially ~5.5 and steadily decreases to a constant value of ~3.0 over a period of ~1 week. At this point such a solution contains excess ^{15}N-MeImH$^+$ and significant amounts of three Pt(II) species, viz., **3**, **5**, and a third species which we believe is ^{15}N-enPt$(H_2O)(^{15}N\text{-MeIm})^{2+}$ (**4**). A proton-decoupled ^{15}N spectrum of such a solution is shown in Figure 1B. The ^{15}N shifts and coupling constants for all of the ^{15}N-enPt(II) species in Figure 1 are summarized in Table I which also includes ^{15}N NMR data for the species **1**, **2**, and **6**.

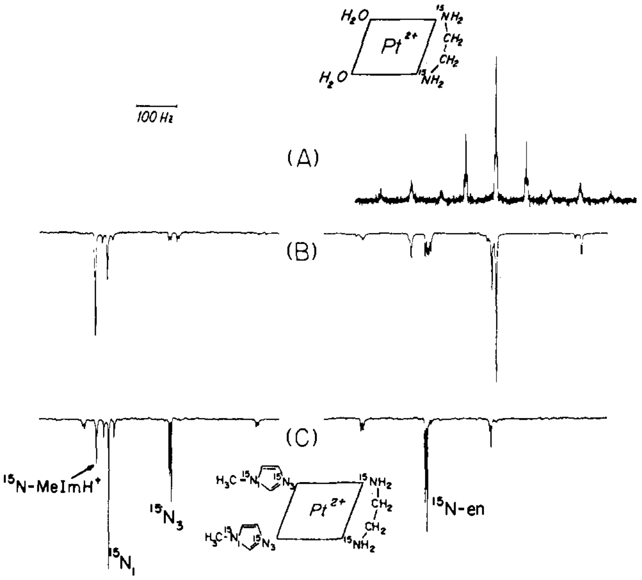

Figure 1. ^{15}N spectra of ^{15}N-en Pt(II) species at 25 °C (the ^{15}N-en spectral features are ~150–200 ppm upfield of the ^{15}N-MeIm region): (A) proton-coupled spectrum of ~0.2 M aqueous solution of ^{15}N-enPt$(H_2O)_2^{2+}$ (**3**), pH 2.0; (B) proton-decoupled spectrum of solution resulting from addition of ~1 ^{15}N-MeIm per Pt(II) to aqueous solution of **3**, pH 2.9; (C) proton-decoupled spectrum of ~0.2 M aqueous solution of ^{15}N-en Pt(^{15}N-MeIm)$_2^{2+}$ (**5**), pH adjusted to 2.0.

Certain features of the data in Table I should be emphasized. Focusing attention on the ^{15}N shift data, we observe the following. (1) The ^{15}N resonance of the equivalent en nitrogens in **5** is shifted downfield by 17 ppm relative to that in **3** and the ^{15}N resonance for the equivalent NH_3 nitrogens in **2** is 20.6 ppm downfield of that in **1**. Thus, replacement of both H_2O molecules by ^{15}N-MeIm produces a sizable paramagnetic shift in the ^{15}N resonance of the amine nitrogens attached to the Pt(II). (2) In **4** the en nitrogens are no longer equivalent. One of them displays a singlet resonance with nearly the same ^{15}N shift and $^{195}Pt-^{15}N$ coupling as the ^{15}N resonance for the en in **3**, and the other displays a 5-Hz doublet with ^{15}N shift and $^{195}Pt-^{15}N$ coupling comparable with that for the en resonance in **5**. We assume that the singlet is due to the en nitrogen trans to H_2O, while the 5-Hz doublet is due to the one trans to ^{15}N-MeIm in the square-planar complex.[8,9] (3) The N_3 nitrogen of ^{15}N-MeIm experiences a large diamagnetic shift (91-93 ppm relative to that of uncomplexed aqueous ^{15}N-MeIm) when complexed by a *cis*-diamine-platinum(II)$^{2+}$ species.

With regard to the coupling data in Table I, the important results are as follows. (1) The $^{195}Pt-^{15}N$ coupling for the amine nitrogens is easily measured and changes by more than 25% (~100 Hz) when H_2O is replaced by ^{15}N-MeIm in **1** or **3**. The predominant effect is again presumed to be due to substitution in the position trans to a given amine nitrogen. (2) Both N_3 and N_1 of ^{15}N-MeIm display measurable $^{195}Pt-^{15}N$ coupling with the coupling to N_3 being very much larger, as expected. (3) The coupling between the amine nitrogen and N_3 of ^{15}N-MeIm is measurable (~5 Hz), but only a single coupling is observed in **2** or **4**. We assume this to be the coupling between nitrogens which are trans to each other in the square-planar Pt(II) complex and that the cis coupling is too small to be observed (<0.5 Hz).[9] (4) The observation of the directly bonded ^{15}N–H couplings for the amine nitrogens in **1** and **3** demonstrates that exchange of the amine protons with H_2O is slow on the NMR time scale (i.e., a proton resides on an amine nitrogen for ~10 ms or longer between exchanges) when these amines are complexed by Pt(II). This is in contrast to dilute aqueous solutions of the free amine where proton exchange with H_2O is very rapid. This may indicate that availability of the amine-nitrogen lone-pair electrons is important for rapid proton exchange with H_2O, as has been suggested earlier.[10]

Another interesting aspect of the data presented here is a consistent trend in the amine-nitrogen ^{15}N shift and ^{195}Pt–^{15}N coupling constant to lower values on substitution of H_2O by the stronger ligand, ^{15}N-MeIm, at the other Pt(II) sites. A similar effect is seen at the N_3 nitrogen of ^{15}N-MeIm in going from **6** to **5** or **2**. This is consistent with the expectation that replacement of H_2O by the stronger amine ligands would lead to a weakening of the trans Pt–N bond.

Addressing the question of the applicability of ^{15}N NMR to studies of the interaction of *cis*-diamine–diaquoplatinum(II) with biological systems, the data in Table I clearly indicate that such association with imidazole-nitrogen sites would lead to substantial changes in both the ^{15}N shift and the ^{15}N–^{195}Pt coupling for the amine nitrogen in the Pt(II) complex. At the same time, the imidazole nitrogen at the biological site would be expected to undergo a large diamagnetic shift (relative to its resonant frequency in the absence of Pt(II) complexation) and to display ^{195}Pt satellites due to ^{195}Pt–^{15}N coupling. From an experimental point of view, the effects on the amine nitrogens of the Pt(II) complex may be more readily observed since those nitrogens are easily ^{15}N labeled and could probably be observed at millimolar concentrations with state-of-the-art NMR equipment. A possible limitation of this approach might be a lack of specificity in determining the particular kind of biological site attacked by the *cis*-diamine–diaquoplatinum(II) species. We are pursuing this question further by studying the ^{15}N NMR properties of the amine nitrogens in a series of ^{15}N-en-Pt(II) complexes with a variety of ligands at the remaining two coordination sites and will report these results at a later date.

Acknowledgment. We thank Dr. B. B. McInteer and Dr. T. R. Mills of the Stable Isotope Resource at the Los Alamos Scientific Laboratory for supplying the enriched ^{15}N. We also thank Dr. D. L. Williams for synthesizing ^{15}N-enriched ethylenediamine and Dr. T. W. Whaley and R. Walker for synthesis of ^{15}N-enriched methylimidazole. Finally, we thank Dr. John C. Bailar, Jr., for encouragement and helpful discussions.

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(9) To our knowledge, no experimental evidence has been provided which demonstrates that spin–spin coupling in a square-planar complex is larger for trans ligands than for cis. We hope to provide experimental confirmation of this assumption by examining the ^{15}N NMR parameters of the species dienPtX^{2+} (dien = diethylenetriamine = $H_2N(CH_2)_2NH(CH_2)_2NH_2$; X = H_2O, MeIm) in which all three dien nitrogens would be ^{15}N labeled.
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Mohammed Alei, Jr.,* Phillip J. Vergamini
William E. Wageman
Los Alamos Scientific Laboratory
University of California, Los Alamos, New Mexico 87545

Received March 9, 1979

Reactions at the Rhodium Vertex of a Rhodacarborane Cluster. Preparation, Crystal and Solution Structure, and Reactions of 3,3-$(Ph_3P)_2$-3-(HSO_4)-3,1,2-$RhC_2B_9H_{11}\cdot O(C_2H_5)_2$

Sir:

Since our discovery[1] that the hydridorhodacarborane 3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_{11}$ (I) is an active catalyst for the isomerization and hydrogenation of olefins, we have explored the extensive chemistry of this cluster in depth, particularly with regard to the Rh vertex. As an example, the reaction of I with sulfuric acid generates H_2[2] and a novel metallocarborane species $(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}$ (II). The addition of hydrogen gas or primary alcohols to solutions of II regenerates I, with accompanying elimination of sulfuric acid from the cluster. We report here the synthesis, crystal and solution structure, and reactivity of 3,3-$(Ph_3P)_2$-3(HSO_4)-3,1,2-$RhC_2B_9H_{11}\cdot O(C_2H_5)_2$ (II). It is of note that II represents the first reported metallocarborane containing a metal–oxygen bond.

To a solution of 2.0 g (2.62 mmol) of I in 100 mL of dichloromethane, 3 mL of H_2SO_4 (50 mmol) was added with rapid stirring. Evolution of H_2 was evident within 30 s and an orange precipitate formed. After 15 min the precipitate was separated by filtration, washed with CH_2Cl_2, and triturated with diethyl ether to produce bright orange crystals of II in 56% yield. Recrystallization from tetrahydrofuran (THF)–heptane affords $(Ph_3P)_2(HSO_4)RhC_2B_9H_{11}\cdot OC_4H_8$. Anal. Calcd for $C_{42}H_{50}B_9RhP_2SO_5$: C, 54.30; H, 5.42; B, 10.47; Rh, 11.08; P, 6.67; S, 3.45. Found: C, 54.51; H, 5.71; B, 10.66; Rh, 11.29; P, 6.47; S, 3.42.

The 200-MHz ^{1}H NMR of II in Me_2SO-d_6 shows a complex multiplet centered at δ 7.6 (area 30) due to the Ph_3P ligands and a singlet at 5.45 (2) assigned to carborane C–H. Multiplets present at 3.55 (4) and at 1.75 (4) are due to the two sets of methylene protons present in OC_4H_8.

The 80.5-MHz $^{11}B\{^1H\}$ NMR is uninformative, consisting of two broad resonances centered at −9 and +5 ppm relative to $BF_3O(C_2H_5)_2$. The 81.02-MHz $^{31}P\{^1H\}$ NMR in THF/Me_2SO (Figure 1) is temperature dependent and is discussed below. The infrared spectrum of II (Nujol) exhibits a band characteristic of terminal B–H bonds at 2550 cm^{-1} in addition to absorbtions due to the coordinated dicarbollide and triphenylphosphine ligands. Three bands at 1150, 1050, and 800 cm^{-1} are assigned to the bisulfate ligand.

II was found to react readily with H_2 gas to regenerate I and H_2SO_4. A solution of II, 200 mg (0.215 mmol) in 100 mL of THF, was treated with hydrogen gas (1 atm) for 10 min. An equal volume of water was added and the acid liberated was titrated potentiometrically with NaOH, giving an equivalent weight of 963 for II, calcd 931. Evaporation of the THF provided crystals of I in 82% of isolated yield. When deuterium gas was used,[3] I could be isolated in high yield and contained only a trace of Rh–H by IR (ν_{RhD} 1520 cm^{-1}). Similarly, II reacted rapidly with ethanol or propanol at 50 °C to produce I in quantitative yield and acetaldehyde or propionaldehyde,[4] respectively.

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