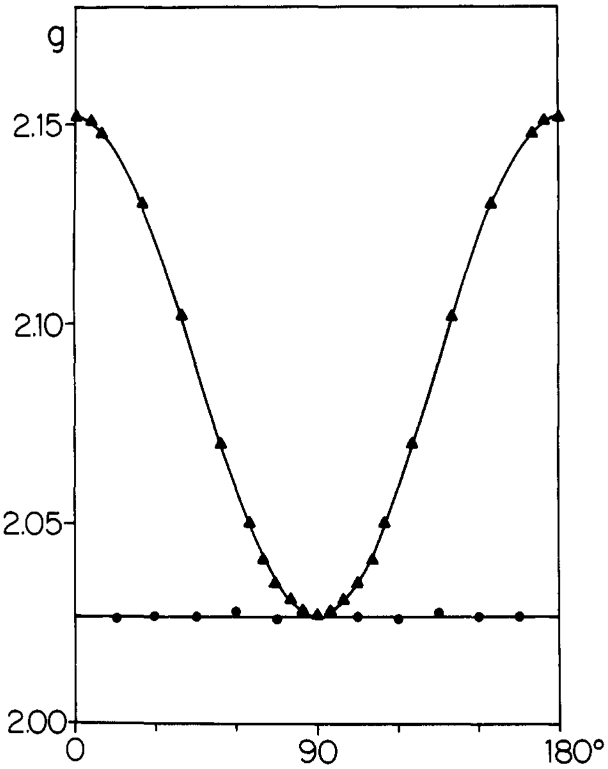

Figure 1. Angular variation of g values for the major copper(II) site in a γ-irradiated Cu(thioacetamide)Cl single crystal at 77 K. Rotation about the crystal c axis (perpendicular to the applied field) denoted by the points ●, rotation about the axis perpendicular to the (±110) faces by the points ▲.

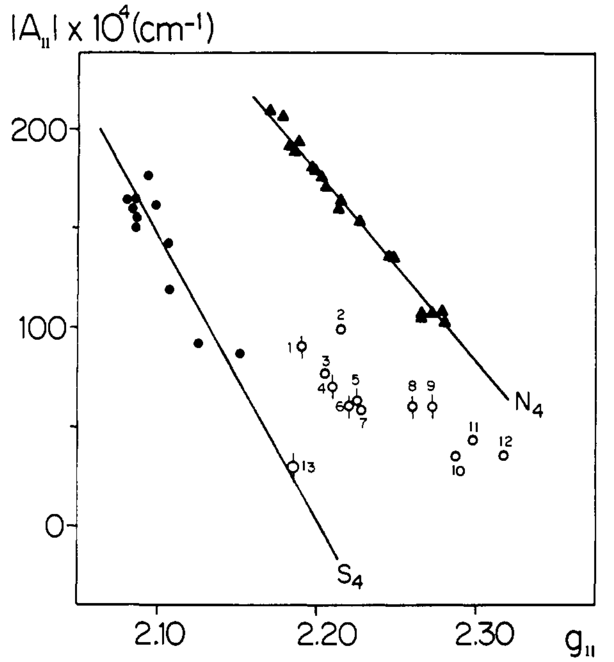

Figure 2. Schema of $g_{\parallel}$ vs. $|A_{\parallel}|$ for CuS_4, CuN_4, and blue protein copper centers. The CuN_4 line is based on data for pyrrole-2-aldiminate and dipyrromethenate copper(II) chelates.[16] The open circles are data taken from ref 6a for blue copper proteins: 1, *P. versicolor* laccase; 2, 3, human ceruloplasmin components; 4, *R. succedanea* laccase; 5, spinach plastocyanin; 6, *C. sativus*, and 7, zucchini ascorbate oxidases; 8, *P. aeruginosa* azurin; 9, *B. pertussis* azurin; 10, *R. vernicifera* stellacyanin, and 11, laccase; 12, horseradish umecyanin; 13, cytochrome-*c* oxidase (from data given by F. T. Greenaway, G. Vincow, and S. H. P. Chan, the 172nd National Meeting of the American Chemical Society, San Francisco, Calif., Aug 29-Sept 3, 1976).

of a tetrahedral copper geometry in blue copper proteins, *as opposed to* a square-planar geometry. Further, Figure 1 suggests that the ESR parameters of blue copper centers are compatible with CuS_2N_2 or $CuSN_3$ coordination, although the low value of $|A_{\parallel}|$ found in such systems is not accounted for by a charge, tetrahedral distortion, or environmental effect *alone*. The lower symmetry associated with an N_2S_2 or N_3S donor atom set may contribute.

We note that Figure 2 corroborates the assignment of pseudotetrahedral CuS_4 coordination in Cu^{2+}-doped tetramethylthiouram disulfide.[19]

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Direct Stacking and Metal–Metal Interactions in Dithioacetato Palladium(II) Complexes

Sir:

Multinuclear d^8-d^{10} metal ion complexes with sulfur-containing ligands are receiving considerable interest.[1] The wide variety of metal-metal interactions and of structural types which is being found in this class of compounds has important implications to topics such as the localized bonding description of the M–M interactions, the nature of the factors influencing M–M bond formation, the consequences of the M–M bond on the overall stereochemistry and electronic structure of the molecules etc.

Our present understanding of the M–M bonding in compounds of this type has been summarized by Fackler[1] recently. Previous work in the field from these laboratories has centered on nickel(II) dithiocarboxylates.[2,3]

We have now obtained the dithioacetato derivatives of

Table I. Principal Intramolecular Distances and Angles, with Standard Deviations in Parentheses, in the Mono- and Binuclear Units of the A Form of $Pd(CH_3CSS)_2$

Distances	Å	Angles	Degree
Pd(1)-S(1)	2.333(6)	S(1)-Pd(1)-S(2)	73.7(2)
Pd(1)-S(2)	2.330(5)	S(1)-Pd(1)-S(1)′	106.3(2)
Pd(2)-S(3)	2.308(7)	S(2)-Pd(1)-S(2)′	106.4(2)
Pd(2)-S(4)	2.309(7)	S(3)-Pd(2)-S(5)	90.9(4)
Pd(2)-S(5)	2.330(8)	S(3)-Pd(2)-S(6)	89.1(3)
Pd(2)-S(6)	2.333(7)	S(4)-Pd(2)-S(5)	89.2(4)
Pd(2)-Pd(2)′	2.755(2)	S(4)-Pd(2)-S(6)	90.6(3)

palladium(II) and platinum(II). For both the metal ions we could isolate several forms, which, although corresponding to a common 2:1 ligand to metal ratio, exhibit different structures. Well-defined spectroscopic variations accompany the structural changes. We present herein a preliminary account of the preparation and of some properties of three palladium(II) derivatives, along with preliminary x-ray data for two of them.

Brick-red, monoclinic crystals (form A) of composition $Pd(CH_3CSS)_2$ have been isolated following reaction of K_2PdCl_4 with CH_3CSSH (1:2 molar ratio) in anhydrous ether and subsequent crystallization from benzene.

Upon dissolution of A in carbon disulfide at room temperature, a red solution is obtained which almost instantly becomes turbid; in a few minutes, a green microcrystalline material (B) separates. Crystals of larger size, suitable for x-ray diffraction studies, have been obtained either upon addition of carbon disulfide to a benzene solution of A or by crystallization of A from 1:3 carbon disulfide-toluene solutions.

A and B are transformed into a third red species (C) upon sublimation at 190 °C and 10^{-3} Torr. B separates from carbon disulfide solutions of C, but, unlike those of A, they keep clear and require several hours (~4) to form the first green microcrystals at room temperature. C analyzes as $Pd(CH_3CSS)_2$ while several analyses, performed on samples of B from different preparations, gave an empirical formula in acceptable agreement with $Pd(CH_3CSS)_2 \cdot \frac{1}{2}CS_2$.

A comparison of the electronic spectra of A, B, and C (reflectance and Nujol mulls) between themselves and with those of other dithiocarboxylates known to contain square-planar $[PdS_4]$ chromophores, e.g., $Pd(C_6H_5CSS)_2$,[4] is of interest. The spectrum of A shows a weak, uncertain shoulder at 17.5 kK and well-defined maxima at 20.0 and 23.0 kK; additional, more intense, bands are found at 29.2, 30.5, 33.6, 34.8, and 40.5 kK. Form B exhibits a sharp maximum at 16.3 kK and two bands, corresponding to those at 20 and 23 kK of A, at 22.2 and 25.0 kK, respectively. The bands beyond 25 kK are little changed, if any, with respect to those of A: 29.2, 33.9, 34.4, 40.7 kK. Form C shows three close maxima at 19.5, 20.7, and 22.1 kK, a weak shoulder at ~25 kK, and ultraviolet bands with maxima at 31.1, 33.9, 37.7 and 39.4 kK. These spectra fall in the range of the known spectral patterns of square-planar sulfur-bonded palladium(II) complexes (e.g., $Pd(C_6H_5CSS)_2$,[5] 18.2, 22.2, 24.0, 26.0, 31.0, 33.5 kK; $Pd(C_6H_5CH_2CSS)_2$,[5] 22, 25.0, 33.5, 34.7 kK), thus indicating that the structures of A, B, and C are based upon approximately square-planar chromophores. On the other hand, the differences among the lower energy transitions (the most likely to contain appreciable metal orbital contributions) of A, B, and C suggest significant structural changes. This suggestion is reinforced by the different multiplicity of ligand bands in the vibration spectra of the complexes.

The preliminary results of two x-ray analyses, carried out on A and B, substantiate the spectroscopic findings. A crystalizes in the monoclinic space group $C2/c$, B in the tetragonal space group $P4/ncc$. Crystal data: A, $a = 9.553 \pm 0.002$, $b = 17.875 \pm 0.002$, $c = 16.141 \pm 0.002$ Å, $\beta = 107.3 \pm 0.1°$, $Z = 12$; B, $a = 12.803 \pm 0.002$, $c = 11.995 \pm 0.002$ Å, $Z = 8$.

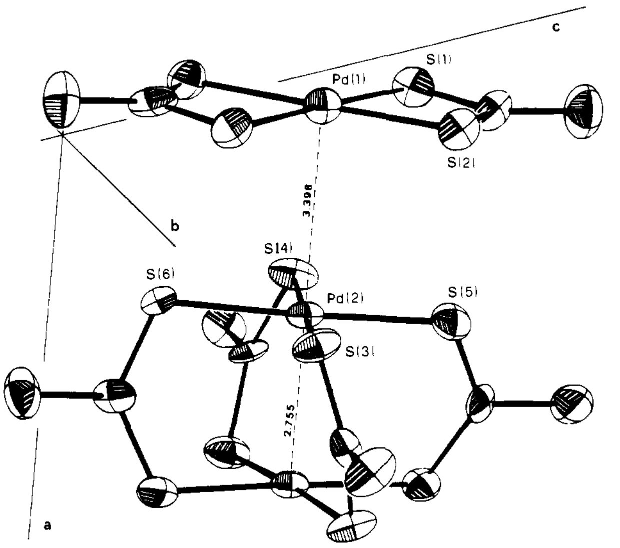

Figure 1. Structure of the A form (see text) of palladium bis(dithioacetate).

The structure of A,[6] shown in Figure 1, consists of mononuclear and binuclear units which alternate along the *a* axis, with the S_4 planes almost parallel. Some intramolecular distances and angles are listed in Table I. The Pd-Pd distance between two different units is 3.398 ± 0.002 Å; this may be compared with those (3.25-3.63 Å) reported[7,8] for palladium compounds of "columnar" structure such as the bis(2,3-butanedionedioximato) or the tetracyano complexes. Other intermolecular contacts in A are in the range of normal van der Waals distances. The monomeric units lie on crystallographic 2-fold axes and are nearly planar (maximum deviation from the least-square plane is 0.02 Å). In the dimer, containing four bridging ligands, the two nearly parallel PdS_4 squares, related by 2-fold axis, are rotated 21° in a tetragonal twist from the eclipsed D_{4h} structure. The Pd-Pd distance in the dimer is 2.755 Å, 0.14 Å shorter than the distance between the centers of the S_4 planes. This M-M distance is even shorter than those found[9] in palladium and platinum bis(ethylene-1,2-dithiolene), 2.79 and 2.77 Å, respectively, which have been taken as examples of direct M-M bonding. Two features in the molecular arrangement of A are unusual for d^8 complexes with sulfur ligands and may have significant implications to both the understanding of bis(1,1-dithiolato) structures and to metal-metal bonding: (i) the stacking in columns with the metal atoms directly over each other and metal-repeat separations of 3.398 and 2.755 Å; (ii) the coexistence of monomers and dimers in the same structure, with different bonding within the chelated rings (for example, the ∠SPdS angle is 73.7° in the monomer and 89.9° in the dimer). This raises interesting questions as to the energetics of the M-M interactions within the dimer and along the columns. It is relevant that in the structure of B,[10] which is built up of only dimers stacking in columns along the 4-fold axes, the M-M distances within and between the dimers are 2.739 ± 0.002 and 3.257 ± 0.002 Å, respectively, both shorter than the distances along the columns of A. In B, CS_2 molecules are incorporated between different columns. The dimers contain four bridging ligands, as in A.

Complete structural information on A, B, and, hopefully, C will be reported subsequently, together with more detailed spectroscopic data and with the results of solution studies, which are in progress. We are also investigating the multinuclear dithioacetato derivatives of platinum(II), copper(I), and gold(I).

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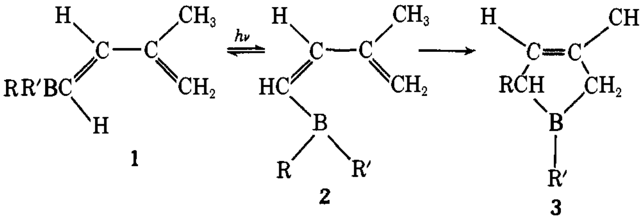
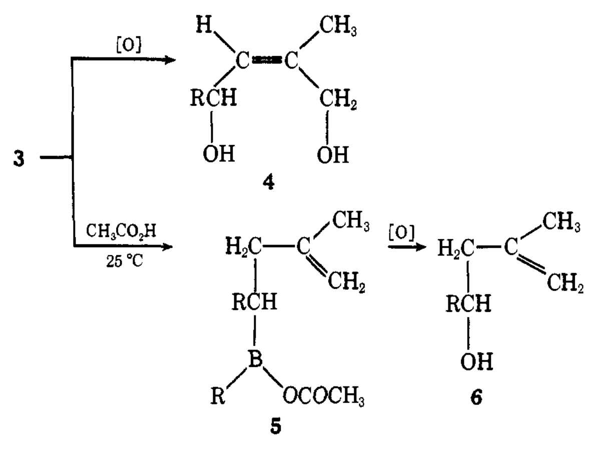
Boracyclopent-3-enes from Dialkyl-1,3-dienylboranes. A Convenient Stereoselective Route to Homoallylic Alcohols

Sir:

Ultraviolet irradiation of dicyclohexyl-3-methyl-*trans*-1,3-butadienylborane (**1**, R = R′ = cyclohexyl) effects its cyclization to the boracyclopent-3-ene **3**.[1] This transformation has been rationalized as occurring via initial excited state trans–cis double-bond isomerization to *cis*-dienylborane **2**, which then undergoes cyclization with transfer of one cyclohexyl group from boron to the adjacent carbon.





R = alkyl, cycloalkyl: R′ = alkyl, cycloalkyl, or 1,1,2-trimethylpropyl

We now wish to report further studies of this photochemical reaction which have shown its great versatility with respect to the structural variations which can be accommodated in both the dialkyl- and dienylboryl moieties. Also, we have now discovered that nonphotochemically generated *cis*-1,3-dienylboranes undergo facile thermal cyclization to boracyclopent-3-enes, which represents a new process in organoborane chemistry. Finally, the boracyclopent-3-enes produced by either the photochemical or nonphotochemical routes from 1,3-dienylboranes may serve as precursors for stereoselective syntheses of homoallylic alcohols. Specifically, the described reactions of dienylboranes derived from isopropenylacetylene might prove to be useful in terpene synthesis for extending a carbon chain by one isoprene unit as indicated in the transformation **1** → **6**.

In a study to determine both the scope of the photoinitiated cyclization reaction and the stereochemical fate of the migrating group, a 0.2 M solution of bis(*trans*-2-methylcyclohexyl)-3-methyl-*trans*-1,3-butadienylborane (**1**, R = R′ = *trans*-2-methylcyclohexyl)[2] in THF was irradiated with an unfiltered 450-W Hanovia lamp for 6 h. NMR examination of the photolysate revealed complete conversion to **3** as evidenced by the disappearance of the dienylborane's terminal methylene proton absorption at δ 5.3 and the simultaneous appearance of a new multiplet at δ 5.5.[3] Acetolysis of the photolysate led to a product whose ^{1}H NMR spectrum exhibited an absorption at δ 4.7, pointing to the presence of terminal vinyl protons as in **5**. Oxidation of the acetolysis reaction mixture with alkaline hydrogen peroxide afforded a 66% isolated yield of a mixture of diastereomeric homoallylic alcohols **6** (R = *trans*-2-methylcyclohexyl).[4,6] Consequently, migration of the 2-methylcyclohexyl moiety from boron to the adjacent carbon must have proceeded with complete retention of configuration.[7]

It should be noted that the synthesis of homoallylic alcohols by this procedure results in the use of only one of the two alkyl groups of the dialkylborane used in the hydroboration step. Fortunately, this problem can be circumvented by using thexylalkylboranes[8] as hydroborating agents. Thus, photolysis of thexyl(2-methyl-1-pentyl)- or thexylcyclopentyl(3-methyl-*trans*-1,3-butadienyl)borane (**1**, R = 2-methyl-1-pentyl or cyclopentyl; R′ = thexyl) resulted in the nearly exclusive migration of the primary and secondary alkyl groups, respectively. This was evidenced by the conversion of the photoproducts to 2,6-dimethylnon-1-en-4-ol and 3-methyl-1-cyclopentylbut-3-en-1-ol, respectively, upon sequential treatment with acetic acid and alkaline hydrogen peroxide.

To establish the scope of the photoinitiated cyclization reaction with respect to the dienyl moiety, 1-ethynylcyclohexene was hydroborated with disiamylborane (bis(1,2-dimethylpropyl)borane). Irradiation for 20 h of the dienylborane **7** (R = R′ = 1,2-dimethylpropyl) formed resulted in its conversion to the photoproduct **8**, whose NMR spectrum exhibited a multiplet at δ 5.4. Acetolysis of the photolysate followed by oxidation produced the corresponding alcohol **9** (R = 1,2-dimethylpropyl), indicating that protonation of the bis-allylic