

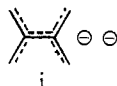
monoanion derivative, in this case 1-propylpentadienyllithium. For comparison purposes, 1-propylpentadienyllithium was generated⁷ from 1,4-octadiene⁶ and gave the same products obtained from III but in different yields: 45, 45, 5, and 5% (sum of last two products), respectively. Protonation of III gave exactly analogous products with protons instead of ethyl groups, in quite different yields:¹¹ 12, 9, 9, 56, and 14%, respectively. Interpretation of the dialkylation and diprotonation results on III may be complicated by the presence of more than one shape of III, the equilibration of these shapes during the first alkylation, formation of monoanions other than the predominant one, and equilibration of the various shapes of the monoanion before and during the second alkylation. Still, the finding that the predominant product from dialkylation has the *Z* configuration and that from diprotonation *Z,Z* seems to offer some support for the nmr evidence above that III has predominantly the *Z,Z* configuration as depicted.

In Table I are included the results of INDO-MO energy calculations for delocalized di- and trianions; there is some correlation between expected stability of the dianion and relative amounts of mono- and dialkylation.¹² In summary, the current findings support extra resonance stabilization for the "Y-aromatic" system I and the homoaromatic homocyclooctatetraene dianion but show that related but nonaromatic systems possessing less stabilization can still be prepared by allylic metalation. The structure and synthetic utility of these and related metalation products are being further investigated.

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(11) Alkylation of pentadienyl anions has previously been observed to give a higher percentage of reaction at the central atom than protonation: R. B. Bates, S. Brenner, C. M. Cole, E. W. Davidson, G. D. Forsythe, D. A. McCombs, and A. S. Roth, *J. Amer. Chem. Soc.*, **95**, 926 (1973).

(12) III-V represent three of the four possible C₆H₈ dianions comprised of sp² hybridized carbons. The fourth, i (binding energy,



–5.756 au; delocalization energy, 1.9β), is unfortunately inaccessible by dimetalation of an *unconjugated* diene.

R. B. Bates,* W. A. Beavers
M. G. Greene, J. H. Klein

Department of Chemistry, University of Arizona
Tucson, Arizona 85721

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Structure of a σ -Carboranyl Complex of Platinum (II), 1-[(P-*n*-Pr₃)Pt^{II}(P-*n*-Pr₂CHCH₂CH₃)]-2-C₆H₅-1,2-

(σ -B₁₀C₂H₁₀). An Unusual Metal-Phosphine Bonding

Sir:

Recently it has been shown that coordination of carborane ligands to transition metal atoms may give

both π - and σ -bonded^{2,3} complexes. In the second case, besides the metal-carbon σ bond,² the metal-carborane coordination is also provided by a M···H-B bridge. On the other hand this kind of bonding may be interpreted in terms of a donation of electrons from a suitable hybrid orbital of the metal atom into an empty orbital delocalized on the C-B-H carborane atoms.² So far no structural evidence has been reported for a "pure" metal-carbon σ bond. Recently Bresadola, *et al.*,^{4,5} have synthesized and characterized a series of platinum(II) and palladium(II) complexes, containing tertiary phosphine and carborane or neo-carborane ligands, which they claim to be the first example of σ -bonded carboranyl complexes. Furthermore they reported that the complexes, obtained from Li-carborane derivatives and *trans*-Pt^{II}Cl₂(trialkylphosphine)₂, achieve four-coordination by internal metallation of one alkyl group of one-coordinated phosphine, involving the second carbon atom of the alkyl group.

In order to find an answer for both problems, we have performed the crystal structure determination of the reaction product between 1-lithium 2-phenyl-1,2-dicarbasododecaborane(12) and *trans*-dichlorobis(tri-*n*-propylphosphine)platinum(II). Details of the crystallographic results are as follows. The crystals were triclinic, with cell parameters $a = 11.77 \pm 0.01$ Å, $b = 10.20 \pm 0.01$ Å, $c = 15.84 \pm 0.01$ Å, $\alpha = 82.5 \pm 0.1^\circ$, $\beta = 95.2 \pm 0.1^\circ$, and $\gamma = 106.5 \pm 0.1^\circ$. Space group $P\bar{1}$ was determined from structure refinement. The density, 1.36 ± 0.01 g/cm³ as determined by flotation, is in agreement with the calculated value of 1.35 g/cm³ with two formula units C₂₆H₅₆B₁₀P₂Pt in the unit cell.

Intensity data were collected by use of a Siemens automated diffractometer with Mo K α -filtered radiation and the θ - 2θ scan technique. Independent reflections (3407), up to $\theta = 25^\circ$, with $I > 3\sigma_I$, were corrected for Lorentz and polarization factors. Although the absorption coefficient is 42 cm⁻¹, no correction was applied because of the small size of the crystal used (nearly a cylinder of 0.2 mm diameter). The structure was determined by the heavy-atom method and refined to a present value of the conventional *R* index of 0.053, by block-diagonal matrix least-squares method with anisotropic temperature factors for the platinum and phosphorus atoms. No peak above 0.6 e/Å³ was detected on the final difference Fourier map.

The platinum(II) atom is coordinated by the carboranyl group through its 1-C atom, by one phosphine through its phosphorus atom, and by the other phosphine through the phosphorus and the first carbon atom of one *n*-propyl side group. The platinum and the four coordinated atoms are coplanar within ± 0.007 Å. A sketch of the molecule is shown in Figure 1, together with some bond lengths of interest.

The structural results confirm (i) the "pure" σ bond between the carboranyl and the metal atom with a Pt-C bond length of 2.13 (1) Å, the carboranyl atoms

(1) G. B. Dunks and M. F. Hawthorne, *J. Amer. Chem. Soc.*, **92**, 7213 (1970), and references therein.

(2) G. Allegra, M. Calligaris, R. Furlanetto, G. Nardin, and L. Randaccio, *Cryst. Struct. Commun.*, **3**, 69 (1974).

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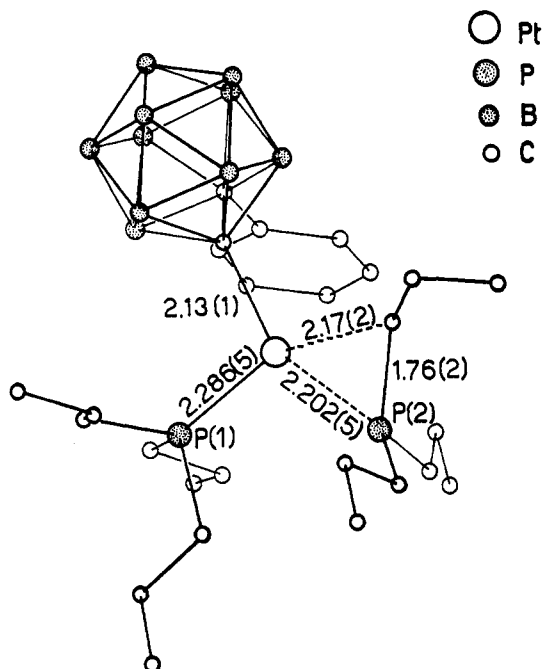


Figure 1. A view of the molecule with some bond lengths and angles of interest. Deviation of individual atoms from their mean plane are Pt, 0.004; P(1), -0.004; P(2), 0.005; C(carb), 0.002; and C, -0.007 Å.

adjacent to the coordinated carbon atom are nearly equidistant from Pt (from 3.31 (2) to 3.43 (2) Å); (ii) the internal metallation involving one alkyl group of the phosphine ligand. However such a metallation does not lead to four- or five-membered rings but involves the *n*-propyl carbon atom bonded to the P atom. Such a three-membered cycle was already postulated by Chatt and Davidson⁶ for the [(Me₂P)₂CH₂CH₂]₂Ru(0).

The geometry of the PtP(2)C cycle may be described by assuming either two Pt-C and Pt-P σ bonds or a π -olefin-like bond between Pt and a P=C double bond. A careful examination shows bond lengths and angles to be in better agreement with the latter bonding scheme. In fact the P(2)-C distance of 1.76 (2) Å is shorter than the other P-C distances which range from 1.82 (2) to 1.89 (2) Å and suggests a significant amount of double bond character. Furthermore the sum of the angles CPC is 342° around P(2) and 308° around P(1). The nonhydrogen atoms of the [(-CH₂)₂P=CHCH₂-] group are almost coplanar. Their mean plane is nearly perpendicular to the coordination plane (see Figure 2). The Pt-P(1) bond length of 2.286 (5) Å appears quite normal for Pt^{II} square planar complexes.⁷ On the other hand, the Pt-P(2) bond length (2.202 (5) Å) is shorter, but it does not dramatically differ from the value reported for Pt-P-*n*-Pr₃ distances,⁸ which range from 2.230 (9) to 2.262 (4) Å. Furthermore, the kind of the bonding of P(1) and P(2) to Pt and their geometries are substantially different. So any comparison of bond lengths may be unreliable.

As far as the *n*-propyl groups are concerned, they have a nearly trans conformation, with the exception of

(6) J. Chatt and J. M. Davidson, *J. Chem. Soc.*, 843 (1965).

(7) G. G. Messmer, E. L. Amma, and J. A. Ibers, *Inorg. Chem.*, **6**, 725 (1967).

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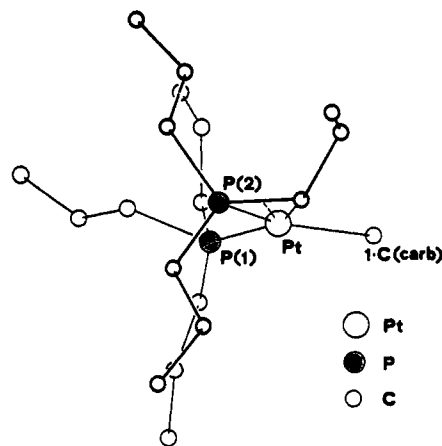


Figure 2. A sketch showing the geometrical relation between the coordination plane and the phosphine ligand bonded to Pt atom through its P and C atoms. Only the coordinated carborane atom is shown.

that involved in the coordination to the metal. In this case the conformation is nearly gauche, the torsion angle being 100.6°, probably due to the steric hindrance of the bulky carboranyl ligand.

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Nevenka Bresciani, Mario Calligaris, Paolo Delise
Giorgio Nardin, Lucio Randaccio*

Istituto di Chimica, Università di Trieste
34127 Trieste, Italy

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On the Blue Shift of the $n \rightarrow \pi^*$ Band of Acetone in Water

Sir:

One of the more dramatic effects of hydrogen bonding is the well-known "blue shift" of the $n \rightarrow \pi^*$ band, observed when a molecule possessing an $n \rightarrow \pi^*$ transition is placed in a hydrogen-bonding solvent. In recent *ab initio* studies of hydrogen bonding between water and formaldehyde, it was found that the calculated energy of the $n \rightarrow \pi^*$ transition in the water-formaldehyde dimer is greater than it is in the monomer, thus reproducing qualitatively the observed blue shift.^{1,2}

In their study of the water-formaldehyde system, Iwata and Morokuma noted that the calculated blue shift in the water-formaldehyde trimer is in rather good agreement with the experimental blue shift of the $n \rightarrow \pi^*$ band of acetone in water. This comparison was interpreted by them as support for the existence of a water-acetone trimer in solution, with the acetone molecule hydrogen bonded at the carbonyl oxygen to two water molecules.¹ A more direct comparison of experimental and theoretical data for the blue shift has not heretofore been possible, due to the experimental difficulties associated with the water-formaldehyde system and the lack of theoretical studies on systems for which experimental data are available.

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(2) J. E. Del Bene, *J. Amer. Chem. Soc.*, **95**, 6517 (1973).