

Figure 2. Linear sweep chronoamperograms of 1.0 mM Tl^+ in 1 M KNO_3 solution on HMDE which was equilibrated with stirred solution for 60 sec at -0.30 vs. sce. Sweep rate = 0.05 V/sec. $[\text{Br}^-] = (\text{A}) 8 \text{ mM}, (\text{B}) 11 \text{ mM}, (\text{C}) 15.5 \text{ mM}$.

Mercury electrodes equilibrated with 1.00 mM Tl^+ and various $[\text{Br}^-]$ at -0.3 V have been further examined with linear sweep chronoamperometry, with results shown in Figure 2. At $[\text{Br}^-]$ below the first Γ_{Tl} discontinuity (curve a), the shape of the Tl^+ reduction wave is little altered. At a $[\text{Br}^-]$ attaining the first Γ_{Tl} discontinuity (curve b), a sharp cathodic current spike appears superimposed on the wave for reduction of diffusing Tl^+ . This spike corresponds to reduction of the adsorbed TlBr crystals over a narrow potential range. As $[\text{Br}^-]$ is increased past the second Γ_{Tl} discontinuity (curve c), a second, more positive, current spike appears on the Tl^+ wave.

The potential sweep results qualitatively demonstrate that the TlBr adsorbed on the two plateaus are electrochemically distinct. Whether the difference in electrochemical properties has kinetic or thermodynamic roots, it clearly must mean that, from the electrode viewpoint, two *structurally* distinguishable kinds of adsorbed TlBr exist on the second Γ_{Tl} plateau.

Two pictures of the adsorbed TlBr could be drawn from the above facts. The pictures differ in whether one supposes a TlBr monolayer or bilayer. In the monolayer picture, we suppose that the second discontinuity in Γ_{Tl} corresponds to some reorientation of the original TlBr monolayer crystal so as to accommodate a large amount of additional TlBr into the monolayer. This monolayer must contain two structurally distinct kinds of Tl^+ .

In the second picture, we suppose that a second monolayer of TlBr is laid on the first. The structural arrangement of the second layer of TlBr surface crystal could be essentially identical with that of the first; the Tl^+ electrochemistries could nonetheless be nonequivalent since the second layer containing Tl^+ is not in contact with the mercury surface and will experience a different potential.

We strongly favor the second, bilayer surface crystal model, both because it requires no new and complex crystal structure for TlBr and because of further considerations of geometrical space requirements. The

values of Γ_{Tl} on the two plateaus in 1 M KNO_3 are 7.2×10^{-10} and 14.8×10^{-10} mol cm^{-2} . It is impossible to accommodate the latter Γ_{Tl} in a single monolayer of composition TlBr. For instance, if TlBr units are arranged perpendicular to the surface, with bromide contacting the surface in a simple cubic packing, a maximum Γ_{Tl} of 11×10^{-10} mol cm^{-2} is estimated for a TlBr monolayer. On the other hand, simple cubic packing of a TlBr monolayer with bond axis parallel to the surface is estimated at 7.4×10^{-10} mol cm^{-2} . Addition of a second layer, staggered over the first to form a (CsCl) body-centered cubic packing, would provide 14.8×10^{-10} mol cm^{-2} for a bilayer of TlBr. (The 110 crystal plane is parallel to the mercury surface.) While such surface space requirement estimations are not proof for the bilayer model, they do show a comfortable accommodation of experimental facts. It also happens that "ordinary" TlBr crystallizes in a body-centered cubic lattice, which was used for the estimation above.

It is evident that TlBr adsorption presents a striking example of surface chemistry. We are undertaking a further thermodynamic and electrochemical characterization of the surface crystals. The potential dependence of K_{surp} is dramatic and consonant with a surface phase formation; see the inset of Figure 1 where Γ_{Tl} is measured as a function of equilibration potential. Finally, the order and spacing of the reduction potentials for diffusing Tl^+ , first monolayer Tl^+ and second monolayer Tl^+ (Figure 2), merits careful study.

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Two-Coordinate Palladium(0) Complexes, $\text{Pd}[\text{PPh}(t\text{-Bu})_2]_2$ and $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$

Sir:

Two-coordinate complexes still remain a rarity in transition metal chemistry. A few two-coordinate d^{10} nickel triad complexes¹ have been reported. None of them, however, has been studied by X-ray analysis. We wish to report here the X-ray structure of $\text{Pd}[\text{PPh}(t\text{-Bu})_2]_2$ (1) and the chemical property along with that of a related complex $\text{Pd}[\text{P}(t\text{-Bu})_3]_2$ (2). A mixture of $\text{Pd}(\eta\text{-C}_3\text{H}_5)$ ($\eta\text{-C}_3\text{H}_5$)₂ and 2 mol of $\text{PPh}(t\text{-Bu})_2$ ³ was stirred in *n*-hexane at room temperature for 4 hr. On cooling the reddish *n*-hexane solution, 1 was separated as diamagnetic pale yellow crystals,⁴ mp 122–126° dec,

(1) See, for example, (a) K. Jonas and G. Wilke, *Angew. Chem.*, **81**, 534 (1969); (b) G. Wilke, M. Englert, and D. W. Joly, *ibid.*, **83**, 84 (1971); (c) P. J. DePasquale, *J. Organometal. Chem.*, **32**, 381 (1971); (d) K. Kudo, M. Hidai, and Y. Uchida, *ibid.*, **56**, 413 (1973); (e) J. Halpern and T. A. Weil, *J. Chem. Soc., Chem. Commun.*, 631 (1973).

(2) B. L. Shaw, *Proc. Chem. Soc., London*, 247 (1960).

(3) B. E. Mann, B. L. Shaw, and R. M. Slade, *J. Chem. Soc. A*, 2976 (1971).

(4) The elemental analysis as well as the molecular weight data conformed reasonably to the respective theoretical values, e.g., Calcd for $\text{C}_{24}\text{H}_{34}\text{P}_2\text{Pd}$ (2): C, 56.40; H, 10.67; mol wt, 510. Found: C, 56.62; H, 10.73; mol wt, 484 (cryoscopic in benzene).

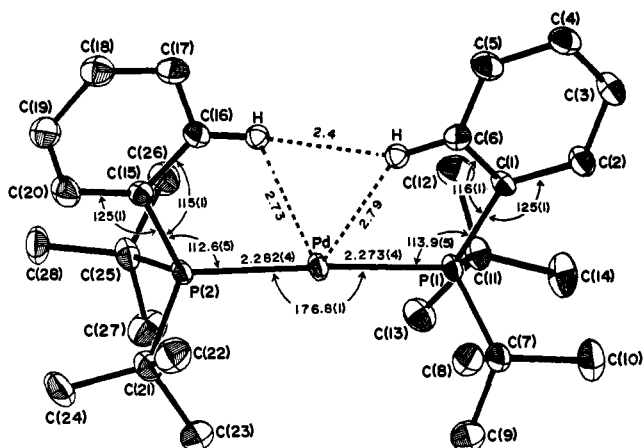


Figure 1. Stereochemistry of and important bond lengths and angles in $\text{Pd}[\text{PPh}(t\text{-Bu})_2]_2$. Hydrogen atom positions are estimated.

in 60% yield. From a similar reaction with $\text{P}(t\text{-Bu})_3^5$ was isolated, upon cooling the solution, **2** as colorless crystals,⁴ mp 160–163° dec, which are very soluble even in paraffinic hydrocarbons.

Crystals of **1** grown from a *n*-hexane solution are prisms developed with the (101) plane: $\text{C}_{28}\text{H}_{46}\text{P}_2\text{Pd}$, $M = 550.99$; monoclinic; space group Cc ; $a = 10.070$ (2), $b = 45.377$ (7), $c = 8.075$ (1) Å; $\beta = 129.84$ (2)°; $Z = 4$; $D = 1.25$ g cm⁻³. Three-dimensional X-ray diffraction data were collected on a computer-controlled Rigaku four-circle diffractometer with a maximum 2θ value of 55° using Zr-filtered Mo $K\alpha$ radiation. The structure was solved by the heavy-atom method and refined by the block-diagonal least-squares method to an R value of 0.062 for 2470 nonzero reflections. Anisotropic thermal vibrations were assumed for all the non-hydrogen atoms. A difference Fourier map did not reveal definitely all the hydrogen atoms.

The palladium atom assumes a slightly bent (176.8°) linear coordination (Figure 1). The entire molecule has an approximately C_2 symmetry. Remarkably, substituents of the phosphorous atoms form an eclipse conformation with nearly parallel phenyl planes. The two phenyl planes form dihedral angles of 13.7 and 15.5° with the plane involving P–Pd–P atoms. The Pd(0)–P distance of 2.278 Å is unexpectedly short in view of the Pd(II)–P distances (2.30–2.338 Å) found in, e.g., $\text{PdI}_2(\text{PPhMe}_2)_2$,⁶ $\text{PdI}_2(\text{PPh}_3)_2$,⁷ and $\text{PdCl}_2(2\text{-phenylazophenyl})(\text{PEt}_3)_2$.⁸ An account for these peculiar features may be found in the proximity of two ortho hydrogen atoms of the phenyl groups. Assuming the conventional aromatic C–H bond length (1.08 Å) and the absence of significant deviation from the normal phenyl geometry, the Pd–ortho hydrogen distances are estimated to be 2.79 and 2.73 Å. These values may be compared with the estimated metal–ortho hydrogen distances 2.84 and 2.85 Å for $\text{PdI}_2(\text{PPhMe}_2)_2$ or 2.59 Å for $\text{RuCl}_2(\text{PPh}_3)_3$.⁹ The distance between two ortho hydrogen atoms is then estimated to be ~2.4 Å. This distance roughly corresponds to the sum of the van der Waals radii of H atoms implying the existence of an

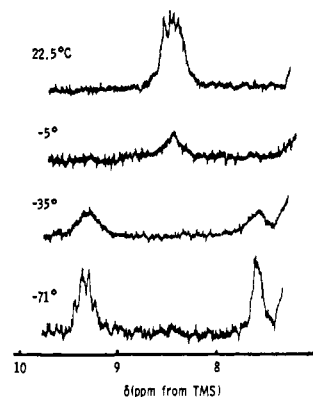


Figure 2. Temperature variant ^1H nmr of ortho protons in **1**.

attraction between the two atoms.^{10a} This reflects on the geometry around the phenyl carbons C(1) and C(15) (see Figure 1). If the two hydrogen atoms experience a repulsive force, this repulsion would easily be removed by rotations of the P–Pd bonds and of the P–aromatic carbon bonds as well. The geometry observed suggests involvement of the metal atom in the attractive interaction.^{10b} The Pd–H₂ three-centered nonbonded interaction, albeit weak, appears to be a main cause for the bent P–Pd–P structure and the short P–Pd distance.

Prolonged heating of **1** (20 hr at 100° in toluene) results in the decomposition producing metallic palladium and no evidence is obtained for ortho-C metallation. Support for the three-centered attractive interaction is obtained from the temperature variant ^1H nmr observed for the ortho protons (Figure 2) which can be interpreted in terms of restricted rotation of the phenyl rings. The enormous deshielding (δ , ppm from TMS, 9.33) observed for one of the ortho proton signals, compared to the others (δ 7.55), reflects the proximity between the hydrogen atom and the metal. The *tert*-butyl protons signal of **1** and **2** is an usual, almost temperature-invariant 1:2:1 triplet (δ (ppm) and $^3J_{\text{H-P}} + ^5J_{\text{H-P}}$ (Hz) are 1.48 and 12.7 for **1** and 1.51 and 12.0 for **2**, respectively).

The bulkiness of $\text{P}(t\text{-Bu})_3$ (the cone angle, $182 \pm 2^\circ$)¹¹ apparently contributes to the unusual stability of **2** toward air. One of the most remarkable features is the fact that under mercury lamp irradiation **2** absorbs hydrogen (normal pressure) at 0° giving polymeric hydride complexes ($\nu_{\text{Pd-H}}$, 2260 cm⁻¹; $\delta_{\text{Pd-H}}$, 847 cm⁻¹). In contrast, complex **1** does not absorb hydrogen but reacts even in solid state with dioxygen giving $\text{PdO}_2\text{-}[\text{PPh}(t\text{-Bu})_2]_2$ ⁴ as stable green crystals: $\nu_{\text{O-O}}$ (Nujol) 915 cm⁻¹; δ 1.47(18 H, d, $J_{\text{H-P}} = 13.2$ Hz), 6.80 (3 H, m), and 7.55 (2 H, m). $\text{CF}_3\text{CO}_2\text{H}$ adds to both complexes affording *trans*-Pd(H)(OCOCF₃)L₂⁴ (L = PPh(*t*-Bu)₂, $\nu_{\text{Pd-H}}$ 2190 cm⁻¹; δ H(Pd) –17.17; $J_{\text{P-H}} = 5.6$ Hz; L = $\text{P}(t\text{-Bu})_3$, $\nu_{\text{Pd-H}}$ 2202 cm⁻¹; δ H(Pd), –18.27; $J_{\text{P-H}} = 4.3$ Hz).

Attempts to prepare nickel analogs from $\text{Ni}(\text{Cod})_2$

(5) H. Hofmann and P. Schellenbeck, *Chem. Ber.*, **100**, 692 (1967).

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(10) (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Interscience, New York, N. Y., 1965, p 433.

(b) On the basis of the Hill's semitheoretical equation^{10a} the van der Waals attractive force exerted between two hydrogen atoms is estimated to be 1.4 kcal/mol, a value too small to account for the observed preference in conformation.

(11) C. A. Tolman, *J. Amer. Chem. Soc.*, **92**, 2956 (1970).

(Cod = 1,5-cyclooctadiene) or $\text{Ni}(\eta\text{-2-methallyl})_2$ have failed.

The propensity of some d^{10} ions, e.g., Ag^+ , Au^+ , and Hg^{2+} , to form two coordination has been ascribed to the large s-p or small d-s separation.^{12,13} Among nickel triad d^{10} systems, two coordination is favored for Pd(0) and Pt(0) in comparison with Ni(0) in this respect.¹⁴ Compared to univalent group Ib metals, e.g., Ag^+ , the energy separations *per se* do not appear to be favorable for Pd(0) to assume a small coordination number. Thus the present examples delineate importance of Pauling's electron-neutrality principle^{15,16} (apart from steric factors) in governing coordination numbers.

(12) R. S. Nyholm, *Proc. Chem. Soc., London*, 273 (1961).

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(14) The d-s separations (eV) are -1.8 (Ni^0), 0.81 (Pd^0), -0.76 (Pt^0), 4.87 (Ag^+), and 1.87 (Au^+), while the s-p separations (eV) are 3.52 (Ni^0), 4.32 (Pd^0), 4.04 (Pt^0), 5.07 (Ag^+), and 5.96 (Au^+). See C. Moore, *Nat. Bur. Stand. (U. S.), Circ., No. 467*, Vol. II, 1952; Vol. III, 1958.

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Multifidene and Aucantene, C_{11} Hydrocarbons in the Male-Attracting Essential Oil from the Gynogametes of *Cutleria multifida* (Smith) Grev. (Phaeophyta)

Sir:

Cellular chemotaxis¹ plays a role in the reproduction of brown algae (Phaeophyta); *i.e.*, the gynogametes (eggs) release volatile substances that act as attractants for the androgametes (sperm). In the isogamous seaweed *Ectocarpus siliculosus*, for example, the sex attractant has been identified as (6*S*)-(cis-1'-butenyl)-1,4-cycloheptadiene (ectocarpene, **4**),² a compound which is also a constituent of the essential oils from vegetative thalli of *Dictyopteris plagiogramma* and *D. australis*.^{3,4} In the oogamous seaweed *Fucus serratus* the male attractant is a 1,3,5-octatriene (fucoserratene).⁵ In this communication we wish to report the isolation and structure determination of the male-attracting substance and a related, biologically inactive compound

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(2) D. G. Müller, L. Jaenicke, M. Donike, and T. Akintobi, *Science*, **171**, 815 (1971).

(3) J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

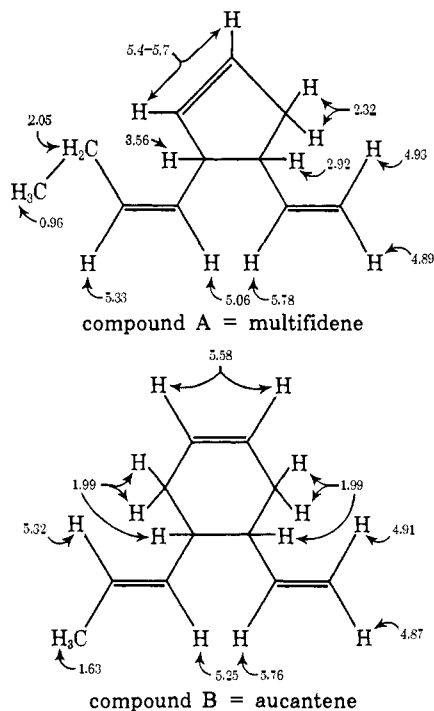
(4) The configuration of C-6 in the Cope rearrangement product of dictyopterene B, (-)-6-(cis-but-1'-enyl)-cyclohepta-1,4-diene, is predominantly R as partial reduction with 1 equiv of diimide produces a small amount of (+)-(S)-6-butyl-cyclohepta-1,4-diene (J. A. Pettus, Jr., Ph.D. Thesis, University of Hawaii, 1971). Dictyopterene D' (ectocarpene) therefore has the S-configuration at C-6.

(5) D. G. Müller and L. Jaenicke, *FEBS (Fed. Eur. Biochem. Soc.) Lett.*, **30**, 137 (1973).

from the anisogamous brown alga *Cutleria multifida* (Smith) Grev. from the Mediterranean coast.

Female plants of *Cutleria multifida* were cultured in the laboratory from unfertilized eggs.⁶ Mature plants were placed in flasks (*ca.* 50 g wet weight in 1-l. sterile sea water per flask) and allowed to release the motile macrogametes into the medium every morning continuously for a period of more than 5 months. The macrogametes were separated from the plants each day by decanting the medium and replacing it with fresh sea water. A stream of purified air was then passed through the suspension of female gametes in the decanted sea water for 24 hr and the volatile material was collected in a Dry Ice cooled trap containing 0.3 ml of fluorocarbon FC-78 (bp 50-60°),⁷ which dissolved the organic material and separated it from the bulk of the condensed water. Subsequent gas chromatography⁸ of this solution on 5% DEGS on Chromosorb P at 65° separated the male-attracting oil into three dextro-rotatory components: 2.5 mg of A, 1.0 mg of B, and 0.2 mg of C from 1 kg of wet seaweed.⁹ Bioassay^{1,6} showed that compound A was responsible for the positive chemotaxis of the male microgametes; compounds B and C possessed no significant biological activity. Compounds B and C were also found to be constituents of the essential oil from the male and asexual plants of *C. multifida*.

Compounds A, B, and C exhibit mass spectra that



are virtually identical with the mass spectrum of **4**, showing that all three components are $\text{C}_{11}\text{H}_{16}$ hydrocarbons and structurally related to **4**. Furthermore all three compounds possess three unconjugated double bonds

(6) Male gametes were exposed to vaseline droplets containing the samples. The halo of gametes around such lures, measured against blanks, is indicative of gamone activity: D. G. Müller, *Biochem. Physiol. Pfl.*, in press.

(7) Obtained from 3M Co., Düsseldorf, Germany.

(8) Compounds A, B, and C have the following Kovats indices on a column of 12.5% Apiezone and 2% Igepal on alkali-washed Chromosorb W: 1056.7, 1086.3, and 1165.0, respectively. The latter is identical with the retention value of ectocarpene (1164.7).

(9) Weights were estimated using *n*-nonane as a reference standard.