

lution. Thus, $|J|$ of $\text{Me}_2\text{Sn}(\text{acac})_2$ in CDCl_3 solution, 966 Hz,⁴ indicates a decrease in θ from 180° in the solid to 161°.⁵ In this way solid-state NMR can help to elucidate solvation and other medium effects.

The magnitude of J in solution has been related to the Sn coordination number (CN)^{4,6} and provides a qualitative probe of organotin(IV) structure. Our data for structurally characterized solids indicate that for tetracoordinated methyltin(IV)s $|J| \leq 430$ Hz, pentacoordinated 470–610 Hz, and hexacoordinated ≥ 630 Hz. However, the NMR data show the relationship of $|J|$ to Sn CN to be indirect. Because of the strong dependence of $|J|$ on θ , greatly distorted tetrahedral, trigonal bipyramidal, or *trans*-dimethyl octahedral geometries may produce values of $|J|$ outside of these ranges and caution should be used when assigning CN on the basis of this criterion.

The Fermi contact term, usually assumed to make the largest contribution to $|J|$ for group 14 nuclei,⁷⁻¹⁰ is a linear function of the electron density at each of the two coupled nuclei¹¹ and reflects the *s*-character of the bonded orbitals. Because the methyl substituent is the same throughout, to a first approximation changes in $|J|$ can be attributed to changes in the Sn contribution. The close dependence of $|J|$ on θ appears to be consistent with the dominance of the Fermi contact term and the substantial, nonzero extrapolated value of $|J|$ for $\theta = 90^\circ$ (150 Hz), where percent *s* character should be zero,¹² may provide an empirical estimate of the contribution of the orbital and dipolar terms to $|J|$.

The different behavior of $\text{Me}_2\text{Sn}(\text{oxinate})_2$ is not readily understood. The Sn–C distance, 2.16 (2) Å,¹³ is intermediate among the hexacoordinated compounds examined. It has been suggested that Sn uses sp^3 -hybridized orbitals to bond to methyl ($\theta = 110.7^\circ$) in this complex^{13,14} but the large deviation from the other $|J|/\theta$ data, and particularly from tetracoordinated methyltin(IV)s Me_4Sn and $[\text{Me}_2\text{SnS}]_3$, suggests that such a simple picture is incorrect. Other hexacoordinated compounds with $\theta < 140^\circ$ will be examined to determine if the deviation is general for contracted Me–Sn–Me bond angles [which could reflect either the importance of the non-Fermi contact terms in determining $|J|$ or a change in Sn hybridization—perhaps the inclusion of *d* orbitals^{8b}—in *cis*-hexacoordinated methyltin(IV)s].

NMR data obtained on structurally characterized compounds must form the basis for examining the structural dependence of NMR parameters. We hope that the availability of these and other $|J|$ /structure data will stimulate theoretical investigations of the J coupling of Sn and other heavy nuclei.

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Formation of Interstitial Pd–C Phase by Interaction of Ethylene, Acetylene, and Carbon Monoxide with Palladium[†]

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Palladium is an important catalyst, widely employed in industrial processes and in the laboratory practice. Its interaction with various gases has been extensively investigated from the point of view of catalytic¹ and surface² properties. Structural changes are known to occur in an hydrogen environment due to formation of palladium hydrides,³ but little attention has been paid so far to changes of the bulk structure of palladium caused by interaction with carbon-containing gas molecules.⁴ Among the catalytically important group 8–10 metals, only Fe, Ni, and Co form stable carbides; reports of palladium carbides^{4b,4c} have not been substantiated.⁵ In this context then, it appears of interest to report that a stable palladium phase, containing up to 13 atom % of carbon, readily occurs on heating metallic palladium in a flow of ethylene, acetylene, or carbon monoxide. Formation, stability, and some properties of that phase are the subject of this paper.

Palladium black (Aesar, Cat. No. 12066) was heated in 50 °C increments in the microreactor of a θ – θ X-ray diffractometer described earlier.⁶ In separate experiments, ethylene, 1% acetylene in helium, and carbon monoxide were allowed to flow through the diffractometer chamber at 40 mL/min. At each temperature 20–30-min diffraction scans were taken. A phase transformation of Pd was observed at approximately 150 °C in C_2H_4 , 250 °C in 1% $\text{C}_2\text{H}_2/\text{He}$, and 500 °C in CO, manifested by an expansion of the Pd unit cell. For example, Figure 1 shows the diffraction pattern of Pd black in a flow of 1% $\text{C}_2\text{H}_2/\text{He}$ at selected temperatures. While there is no change in the structure on exposure of Pd to C_2H_2 at room temperature, a shift of peak positions is noticeable above 100 °C. At 200 °C each reflection is split into two components indicating a coexistence of two phases, both of which show lattice expansion with reference to pure Pd. Only

[†] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The *d*-transition elements comprise groups 3 through 12, and the *p*-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

(1) Literature in this area is voluminous. (a) For recent advances, see the Proceedings of the 2nd European Symposium on Catalysis on Metals, published as: *J. Mol. Catal.* **1984**, *25*. (b) For selected examples of earlier literature, see: Somorjai, G. A. "Chemistry in Two Dimensions"; Cornell University Press: Ithaca, NY, 1981; pp 414–474.

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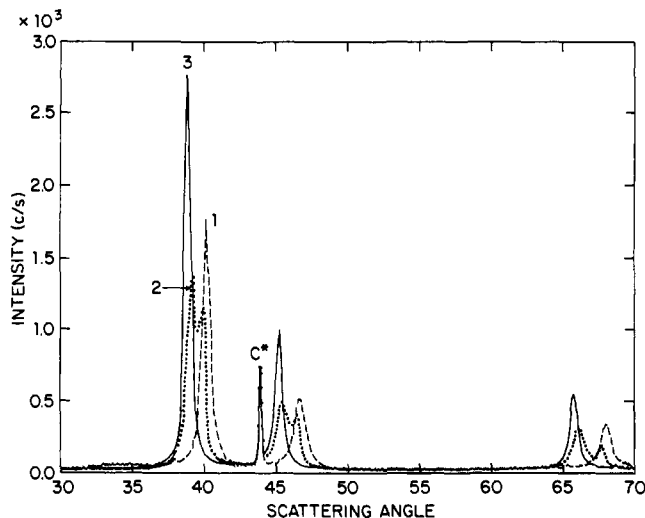


Figure 1. Changes in the X-ray diffraction pattern of palladium black exposed, in sequence, for 20 min to flow of 1% C_2H_2/He at 1–25, 2–200, and 3–300 °C. C* represents the diamond standard.

a single phase is observed at 250 and 300 °C. This phase has an approximate lattice constant of $a_0 = 0.399$ nm, as opposed to $a_0 = 0.389$ nm for Pd.

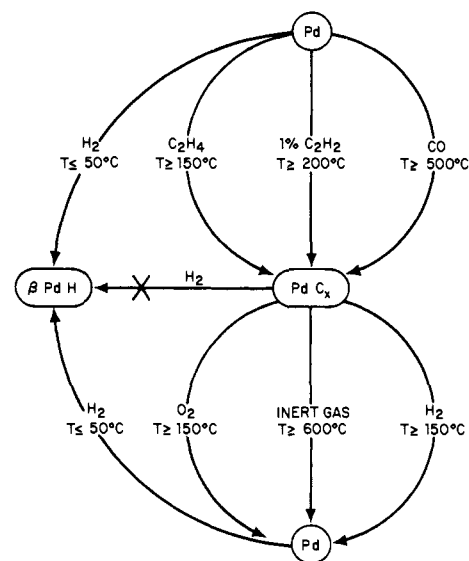
The lattice constant of the carbide phase is, however, somewhat dependent on sample preparation and probably reflects variability in carbon concentration and distribution.

Structural characterization of the Pd–C phase was carried out by Rietveld refinement of neutron diffraction data collected on the General Purpose Powder Diffractometer⁷ at the IPNS facility. The sample for this experiment was prepared by treating palladium black with ethylene for 18 h at 300 °C. Refinement of the data was initially carried out with only the Pd atom (at 0,0,0) which led to a structure-factor R index of 0.373 and a weighted profile R of 0.106. Refinement of potential carbon atoms sites at $1/4, 1/4, 1/4$ and $1/2, 1/2, 1/2$ were then attempted; only the latter was successful, reducing the R indices to 0.162 and 0.061, respectively. The occupancy of this octahedral site was included as a variable in the refinement: for the formulation PdC_x , $x = 0.15(2)$. The isotropic thermal parameters for Pd and C refined respectively to 0.63 (2) and 0.66 (8) Å², while a_0 , the cubic unit-cell parameter, converged at 0.39956 (4) nm.

The sputter depth profiles of C and Pd were obtained by ion scattering with a mixed ^4He-Xe beam at an incident ion energy of 2.0 keV, on the Pd foils (0.1 mm) which were previously exposed to C_2H_4 and C_2H_2 at various temperatures. For the sample treated 100 h in a flow of C_2H_4 at 300 °C a constant C/Pd ratio was obtained throughout the sputtered depth (total ion dose ca. 4×10^{17} cm⁻²). At lower exposures to C_2H_4 (1.5 and 4 h at 150 °C) the same constant C/Pd ratio was found in the near-surface region, but on further sputtering, the C concentration in palladium decreased by more than 1 order of magnitude. The depth of the constant C/Pd region increased with the exposure. Thus, a movement of the carbon diffusion front was detected in palladium.

Higher temperatures are required to induce phase changes of Pd in the carbon monoxide atmosphere. Only at 500 °C is the coexistence of two phases observed, the prevailing one being the Pd–C phase found earlier in C_2H_4 and C_2H_2 . On further heating the composition shifts back to Pd and only Pd reflections are seen at 600 °C. The high temperature at which the Pd–C phase appears in CO is probably related to the nondissociative adsorption of CO on Pd.⁸ At higher temperatures, when C–O bond breaking becomes possible, the surface coverage by CO is low, as judged

Scheme I



from the TPD profile.^{9,2b} Thus the carbon pool on the surface, available for diffusion into the bulk, is much lower at all temperatures than in the case of unsaturated hydrocarbons.¹⁰

Suppression of β -PdH formation in the H_2 atmosphere offers a convenient diagnostic tool for the presence of interstitial carbon in palladium. This can be observed either by X-ray diffraction or by a direct measurement of the hydrogen uptake observed when a Pd sample is cooled from 150 to -20 °C in an flow of 5% H_2/N_2 . The hydrogen uptake measured by the latter technique corresponds to $H/Pd = 0.66$. After pretreatment in flowing ethylene at 180 °C for 2 h, no measurable uptake of H_2 was detected.¹¹ Analogous results were obtained after pretreatment of Pd in CO at 515 °C. Lattice parameters and properties of Pd (β -PdH formation) can be restored by heating the Pd–C phase above 150 °C in H_2 or O_2 or above 600 °C in an inert atmosphere (Scheme I).

In summary, a Pd–C phase, distinct by X-ray diffraction, is formed when palladium is heated in an atmosphere of ethylene, acetylene, or carbon monoxide. This process involves deposition of a carbonaceous overlayer, followed by an activated diffusion of carbon atoms through the metal lattice. The extent of incorporation of carbon atoms in the octahedral sites of Pd is ca. 13 atom %. It is important to note that unlike the X-ray experiments, the unique scattering contrast for neutrons makes this determination a straightforward task. As the consequence of incorporation of carbon, palladium loses its ability to form β -PdH. The Pd–C phase is metastable and decomposes above 600 °C in an inert atmosphere and at ca. 150 °C in H_2 or O_2 .

On the basis of the present results it can be postulated that the Pd–C phase can also occur by interaction of other carbon-containing molecules with palladium. The necessary condition seems to be that such molecules undergo dissociative chemisorption on Pd below the limit of thermal stability of the Pd–C phase.

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