Chemisorption of gaseous molecules, especially hydrogen, is extensively used to estimate the dispersion of group VIII (groups 8–10) metal catalysts. Chemisorption methods are especially important for highly dispersed catalysts, because of the difficulty to establish their dispersion by other techniques, such as X-ray diffraction or electron microscopy. When hydrogen chemisorption data are used to calculate metal surface areas, often a hydrogen-to-metal stoichiometry of one is assumed. However, H/M values exceeding unity have been obtained for supported Pt, Rh, Ir, and Pt catalysts by hydrogen extensively used to estimate the dispersion of group to metal stoichiometry of one is assumed. However, H/M calculated straightforward from the chemisorption results, be-

The results of hydrogen chemisorption and EXAFS measurements were compared for several Pt, Rh, and Ir catalysts supported on SO2, A1203, and TiO2 (Figure 1). Although a variety of supports and pretreatments was used, their effect on the hydrogen-to-metal stoichiometry appeared to be minor, since straight lines were obtained independent of the support used. A large difference was observed between the three metals and for a fixed coordination number H/Pt < H/Rh < H/Ir was observed. Several explanations have been proposed for high H/M values. A common explanation is that part of the hydrogen is supposed to be adsorbed by the support through hydrogen spillover from the metal particles. Since in the case of spillover differences are expected between the supports used, and not between the metals used, spillover cannot explain our observations. Our results have to be explained by an adsorption stoichiometry larger than one. Subsurface hydrogen seems to provide an opportunity for high stoichiometries. However, subsurface adsorption cannot explain H/M values higher than one either, because subsurface adsorption sites need subsurface metal atoms in order to exist. Therefore multiple adsorption on exposed metal atoms, especially at edge or corner positions, must be the main reason for the observed high H/M values.

To explain the observed differences in adsorption stoichiometry for Pt, Rh, and Ir, we have taken the view that the small metal particles (d < 15 Å) can be considered as transition-metal polyhydride complexes. These very small particles consist of too few atoms to be truly metallic. This fact has also been observed by Sanz and Rojo in 'H NMR of hydrogen on Rh/TiO2 (P(H2) > 40 kPa). They found chemical shifts very similar to those of transition-metal hydride compounds. Although transition-metal

Acknowledgment. This work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).
coordination compounds exist with atomic hydrogen as well as with molecular dihydrogen as ligands, only hydride ligands need to be considered, because $\gamma$-$\text{H}_2$ complexes are extremely labile. Recently, Minot et al. performed calculations on the hydrogenation of small Pt, ($n = 2-13$) clusters using the extended Hückel method and reported stable complexes like $\text{Pt}_n\text{H}_4(\text{H}_2)_2$ and $\text{Pt}_n\text{H}_6(\text{H}_2)_3$. Although this suggests that high $\text{H/Pt}$ values may be possible, synthesis of hydride complexes of Pt with $\text{H/Pt} > 2$ has rarely been reported. When Pt, Rh, and Ir are compared, we expect Pt to coordinate less ligands than Rh and Ir in the same oxidation state, because Pt has one electron more. Rh and Ir differ in the fact that higher oxidation states are more stable for Ir than for Rh, and since the $\text{M-H}$ band can formally be described as $\text{M}^+\text{H}^-$, higher $\text{H/M}$ values are expected for Ir. In accordance with this Garlaschelli et al. prepared polyhydride complexes with $\text{H:Ir} = 5$, while the same procedure for Rh yielded only $\text{H:Rh} = 2$. So the $\text{H/M}$ stoichiometries in polyhydride complexes increase in the order $\text{H/Pt} < \text{H/Rh} < \text{H/Ir}$. The results of this study show that hydrogen chemisorption measurements cannot be used directly to determine particle sizes in highly dispersed catalysts. Above $\text{H/M} = 0.7$, the $\text{H/M}_{\text{surface}}$ stoichiometry exceeds unity; below $\text{H/M} = 0.7$, the uncertainty in the metal–metal coordination number is too high to determine the $\text{H/M}_{\text{surface}}$ stoichiometry. However, for one particular metal the hydrogen chemisorption results can always be used to compare metal particle sizes in a qualitative way. By means of the EXAFS technique a calibration can be made, and then $\text{H/M}$ values can be quantitatively related to the percentage of exposed metal atoms. The observed differences in $\text{H/M}$ values for Pt, Rh, and Ir are analogous to the differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes. Details of this and differences in stability of their polyhydride complexes.

The ESCA bands show unambiguously that the ion is not symmetrical. The relationship between the structures can be seen clearly by writing them in the form $2-4$. While $2$ and $4$ are represented, for convenience, as classical carbenium ions, the evidence, as noted above suggests that they are best formulated as unsymmetrical $\pi$ complexes, derived by displacing the apical methylene group in $3$ toward one end or other of the basal $\text{C=C}$ bond.

On the Question of Heavy Atom Tunneling in the 2-Norbornyl Cation

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Received October 24, 1985

The controversy concerning the structure of the 2-norbornyl cation (1) has focused on two questions: (a) Is the ion symmetrical, as indicated in $3^\circ$? (b) If it is unsymmetrical, is it a normal classical secondary carbocation? Chemical evidence and the chemical shifts in its ESCA spectrum suggest that the answer to the second question is "no". Equally, the integrated areas of the ESCA bands show unambiguously that the ion is not symmetrical. The relationship between the structures can be seen clearly by writing them in the form $2-4$. While $2$ and $4$ are represented, for convenience, as classical carbenium ions, the evidence, as noted above suggests that they are best formulated as unsymmetrical $\pi$ complexes, derived by displacing the apical methylene group in $3$ toward one end or other of the basal $\text{C=C}$ bond.

The NMR spectrum of the ion corresponds, however, to a symmetrical structure, even at liquid helium temperature. The only way to reconcile this evidence with the ESCA results is to suppose that $2$ and $4$ interconvert rapidly even at $4 \text{ K}$. Classical interconversion, by crossing an energy barrier, could be fast on the NMR time scale at this temperature only if the barrier height were less than $0.2 \text{ kcal/mol}$. Apart from the improbability of this being the case, it is not clear that so low a barrier would be consistent with the ESCA measurements, given that these were carried out at $77 \text{ K}$ where $kT \approx 0.2 \text{ kcal/mol}$.

A simple solution of this problem was proposed by Fong and by Brickmann, i.e., that the interconversion of $2$ and $4$ takes place by tunneling. While this suggestion has been ignored because of the belief that tunneling involving heavy atoms (heavy atom tunneling, HAT) cannot be fast, Carpenter has recently shown that it can be, and we have confirmed his suggestion. Indeed, using a better procedure, we found the rate of HAT in the system he studied (automerization of cyclobutadiene) to be even greater.

(2) This follows from the chemical shift of the band corresponding to the cationic carbon atom; see: Olah, G. A.; Mateescu, G. D.; Riemenschneider, J. L. J. Am. Chem. Soc. 1972, 94, 2529.