

temperature is caused by the rapid motion of the iron atom around the ring by a 1,2-shift. NMR only "sees" the time arranged environment and if the motion is sufficiently rapid all five protons of the  $\sigma$ -cyclopentadienyl group appear to be equivalent.

A similar situation exists for the cyclo-octatetraene (COT) complexes  $[\text{Fe}(\text{CO})_3(\text{COT})]$  and  $[\text{Ru}(\text{CO})_3(\text{COT})]$ . The X-ray structure of  $[\text{Fe}(\text{CO})_3(\text{COT})]$  shows the iron atom to be bonded to only four of the carbon atoms yet the  $^1\text{H}$  NMR spectrum at room temperature shows only a sharp singlet resonance. As the temperature is lowered the resonance broadens then splits, but even at  $-145^\circ$  is still broad. The ruthenium complex, however, which also shows a singlet resonance at room temperature shows four well-defined resonances at  $-145^\circ$  interpretable in terms of a structure in which the ruthenium is bonded to only four carbon atoms. The computer simulated spectra are only consistent with the ruthenium atom moving around the ring by a 1,2-shift and rule out 1,3; 1,4; 1,5 or random shifts. Professor Cotton went on to discuss some more complex fluxional molecules some of which have been investigated by variable temperature NMR; these include  $[\text{Cr}(\text{CO})_3(1,3,5,7\text{-tetramethylcyclo-octatetraene})]$ ,  $[\text{Fe}_2(\text{CO})_5(1,3,5,7\text{-tetramethylcyclo-octatetraene})]$ ,  $[\text{Ru}_2(\text{CO})_6(\text{COT})]$  and  $[\text{Ru}_3(\text{CO})_4(\text{COT})_2]$ .

### Reactions with Rhodium Chloride

B. R. James, M. Kastner and G. L. Rempel (University of British Columbia) studied the kinetics of reactions between  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$  and ethylene. In non-aqueous solvents such as dimethylacetamide, the anion  $[\text{Rh}^{\text{I}}\text{Cl}_2(\text{C}_2\text{H}_4)_2]^-$  is formed but in water the production of small amounts of rhodium(I) species catalyses the formation of  $[\text{Rh}^{\text{III}}\text{Cl}_2(\text{H}_2\text{O})_7]^+$ . Acetylenes are catalytically hydrated by chlororhodate(III) complexes. The reaction mechanisms all involve insertion of the unsaturated organic molecule (ethylene or acetylene) into a  $\text{Rh}^{\text{III}}\text{-OH}$  bond.

R. Murray and J. Walker (I.C.I. Petrochemical and Polymer Laboratory) have made a thorough 220 MHz. and 100 MHz.  $^1\text{H}$  NMR study of substituted triphenylphosphine complexes of palladium(II) and platinum(II), and corresponding  $^{19}\text{F}$  studies on  $\text{P}(p\text{-FC}_6\text{H}_4)_3$  and  $\text{P}(m\text{-FC}_6\text{H}_4)_3$  complexes. They interpret their results in terms of  $\sigma$ - and  $\pi$ -electronic effects. Our knowledge and understanding of factors contributing towards chemical shifts and spin-spin coupling constants is still limited and only tentative interpretations can be at present given to such studies.

### An Improved Schottky Diode

The conventional Schottky barrier diode (which does not inject minority carriers) is capable of switching times less than 0.1 nanosecond. An improved version has been developed by M. P. Lepselter and S. M. Sze at the Bell Telephone Semiconductor Device Laboratory (*Bell Laboratories Record* 1967, 45 (Nov.), 340). The introduction of a guard ring eliminates "edge effect", giving a breakdown voltage close to the theoretical limit, while the use of a very clean junction between the n-type silicon semiconductor and a layer of platinum silicide provides an almost ideal forward current-voltage characteristic.

The n-type silicon substrate is cleaned by a glow discharge in which gas ions remove impurities by bombardment. Without removal from the vacuum chamber a smooth layer of platinum is then sputtered on. The result is a layer of uncontaminated platinum silicide with a near-perfect interface to the n-type silicon. Successively, a guard-ring of p-type silicon is formed, a silicon dioxide layer deposited, channels of access etched, and gold beam leads applied.

Platinum silicide is a very stable compound, highly resistant to corrosion and able to form a low-resistance contact. In other related applications the silicide layer receives a deposit of titanium followed by a platinum layer. The titanium layer bonds strongly to the silicon dioxide insulating layer, which it improves by absorbing impurities. The further platinum layer is required to form a strong bond with the gold leads, and also to prevent gold/titanium reactions.

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