Relative Signs of $J(^{195}Pt-^{1}H)$ in Olefin Complexes

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Proton magnetic resonance has been extensively used in the investigation of bonding in Pt^{II} olefin complexes.[1–3] Much of the ^{195}Pt—^{1}H coupling data has been interpreted in terms of the Fermi Contact contribution established through a platinum orbital containing some *s*-character and σ–π mixing in the olefin moiety.[4,5] This coupling is observed as satellite peaks on either side of the main proton resonance and is due to the presence of ^{195}Pt which has a spin of $\frac{1}{2}$ and a natural abundance of 33·7%. We have examined a series of compounds of the type Pt^{II}(acac)Cl(olefin) which can exhibit geometrical isomerism (*e.g.*, when the olefin is propene or *cis*-butene) and also chemical shift differences between normally equivalent protons (*e.g.*, when the olefin is ethylene or *trans*-butene). Due to the different steric requirements of Cl and O, we would expect to observe variations in J(Pt–H) due to a twisting of the olefin to minimise nonbonding interactions. Such twisting would permit the protons on one side of the double bond to be closer to platinum than those on the other side. Twisting has been observed previously in *trans*-$Pt^{II}Cl_2L$(olefin) complexes for the propene derivatives.[3,6]

In the present series of compounds, the geometrical isomers (olefin = *cis*-butene or propene) do not occur in equal abundance suggesting that whilst twisting leads to a decrease in steric repulsion it also leads to a decrease in effective Pt–olefin orbital overlap. The relative amounts of isomer may be observed by freezing out the olefin rotation which occurs rapidly enough to coalesce the proton resonances at room temperature. Relative peak heights indicate isomer ratios below the coalescence temperature and the averaged chemical shift above coalescence also permits estimation of the ratio of isomers. The most abundant isomer is assumed to be the one with the least steric hindrance and thus the least amount of olefin twisting. Rationalisation of our data then leads us to the conclusion that whereas ^{195}Pt coupling to the olefin protons (64—75 c./sec.) increases in magnitude with decreasing Pt–H distance, the ^{195}Pt coupling to the methyl protons (29—40 c./sec.) decreases. Spin decoupling experiments revealed that the upper component of the ^{195}Pt doublet of the methyl proton resonances corresponds to the low-field component of that of the olefinic protons, and *vice versa*. This was also observed in the case of derivatives of the type $PtCl_2$(*p*-toluidine)(olefin). Thus *J*(Pt–CH) and *J*(Pt–C–CH) have opposite signs in the Pt^{II} olefin complexes just as in the σ-bonded complex $PtCl(C_2H_5)_3$.[7]

The effect of decreasing the Pt–H distance is therefore to cause an algebraic increase or decrease in both coupling constants. In view of this we suggest that contributions to the coupling other than that of the Fermi Contact Term are important and that caution is necessary in interpreting these constants in terms of *s*-character of the atomic orbitals involved in the bonding. Full details of this work will be presented elsewhere together with kinetic data on the rates of intramolecular rotation of the olefin moiety. The spin decoupling experiments were carried out on a Varian HA 100 spectrometer.

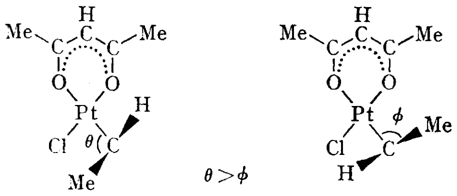

FIGURE. *Representation of isomeric forms.*

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