Transition metal–hydrogen–E (E = C, Si, Sn) three-centre bonds. Towards an NMR measure of the strength of the metal–R3EH interaction

L. Carlton

METHODS OF CHARACTERIZING THREE-CENTRE BONDED TRANSITION METAL–R3EH (E = C, Si, Sn; R = alkyl, aryl) COMPLEXES ARE DISCUSSED WITH A FOCUS ON NMR SPECTROSCOPY AND THE POSSIBLE USE OF NMR TO PREDICT THE STRENGTH OF THE METAL–R3EH INTERACTION.

The derivatization of normally chemically inert hydrocarbons such as methane is a challenge that has exercised the minds of inorganic chemists for many years.1–10 Indeed, it has been identified by some researchers as the ‘Holy Grail’ of organometallic chemistry.1,11 A successful process might mimic the function of the enzyme methane monooxygenase (CH4 → CH3OH at ambient temperature and pressure)12 without necessarily replicating the chemistry. A crucial step in such an activation process is an interaction between the substrate (the alkane) and a catalyst, most usefully a transition metal, that leads to a weakening or breaking of a C–H bond. Where weakening occurs, the interaction is found, in model systems, to take the form of a three-centre bond (for example 11 and 22). Such three-centre bonded complexes are of interest in their own right, since they can provide information about the geometry of the metal–substrate interaction and also (potentially) a means of quantifying factors governing the strength of the interaction.

The structurally characterized transition metal complexes having M–H–C three-centre bonds (for example, 1 and 2) exhibit an interaction in which the bond is supported by one or more additional, conventional bonds between the metal and the hydrocarbon (NMR evidence has shown the existence of short-lived unsupported M–H–C bonds13). Structures of this type have been extensively studied by Green and co-workers,14,15 who have identified them using the term ‘agostic’. A supported three-centre bond is not the best model for an intermediate in a catalytic process, where additional supporting bonds are normally absent. For this reason (among others) analogues of the M–H–C bonded systems containing the group IV congeners silicon17–25, germanium26–31 and tin32–34 have also been studied. The advantages of working with these elements are the higher stability of the unsupported M–R3EH three-centre bond (a consequence of the presence of d orbitals on E) and the higher natural abundance of NMR-active isotopes (in the case of Si and Sn).

The structural characterization of three-centre bonded systems has relied heavily on the use of X-ray diffraction, which suffers from the disadvantage that a hydrogen atom is difficult to detect and locate accurately when in close proximity to atoms having a much larger number of electrons. Far more useful, for this purpose, is neutron diffraction, but here the more stringent requirements in terms of crystal size and limited access to diffraction facilities have inevitably restricted the number of studies. Complex 33 and a number of agostic M–H–C structures35–37 have been characterized in this way.

Complex 4, chemically very similar to 3, was shown some years earlier to have Ph3Si and H bound only weakly, consistent with a three-centre bond. Hart-Davis and Graham38 measured an enthalpy of activation ΔH‡ = 125 kJ mol−1 for the dissociation of Ph3SiH from 4. This is comparable to the dissociation energies of RO–OR and (CO)3Mn–Mn(CO)5, where bond breaking occurs readily on warming.

The vast majority of three-centre bonded systems are unstable, reactive and difficult to isolate and it is unrealistic to hope that diffraction studies are possible in more than a small proportion of cases. Systems amenable to kinetic studies are unlikely to be numerous and measurements will inevitably be very time-consuming. Ideally, a parameter is required that can be obtained in a single simple measurement and, once checked against a calibration graph, will yield a value of ΔH‡ for the M–(R3EH) interaction; such a parameter is the E–H NMR spin-coupling constant. Or, more correctly, the E–H coupling constant is potentially such a parameter, since it is a function of a number of variables, not all of which are related to the strength of the E–H bond.39

The work of Green40 and others41–43 has shown that the presence or absence of a three-centre M–E–H (E = C, Si, Sn) bond is indicated by the magnitude of the E–H spin coupling constant, J(E–H). In a three-centre bonded complex J(E–H) has a value significantly lower than that found for free R3EH but substantially higher than that of the full oxidative addition product H–M–ER3, in which the E–H bond no longer exists.42–43 Three-centre bonds are now commonly reported on the basis of NMR evidence alone. This should not be taken to imply that information about the strength of the M–R3EH interaction can be derived from a measurement of J(E–H) taken in isolation, without reference to other data recorded for the purpose of calibration. The dependence of J(E–H) on the three-centre bond strength will vary on changing M and also on making any major changes to the coordination geometry of M, to the ligands attached to M or to the substituents attached to E.

The strength of a metal–R3EH interaction is influenced by the electron-donating properties of ligands attached to the metal. For example, in complex 5 the interaction between tin and rhodium and between hydrogen and rhodium is strong, whilst that between tin and hydrogen is weak. This is shown by an X-ray study (Sn–H distance 2.31(5) Å) by the magnitude of the tin-hydrogen coupling constant (|J(tin–H)| = 29 Hz)
and by its thermal stability. Complex 6, on the other hand, is unstable at temperatures above 30°C, dissociating with loss of Ph₃SnSH from a kinetic study of its thermal decomposition and an activation enthalpy of ~96 kJ mol⁻¹ has been found. Complex 6 has \( J(197\text{Sn}–1\text{H}) = 106 \text{ Hz} \). The greater nucelophility of 4-dimethylaminoxydine as compared to triphenylphosphine clearly causes a very significant change in the strength of the rhodium–triphenyltin hydride interaction, a change which is reflected in the value of \( J(197\text{Sn}–1\text{H}) \).

Complexes 8 with electron-rich combinations of ligands are more difficult to prepare (in situ) than those with less electron-rich ligands. A number of complexes having the most electron-rich combinations of ligands are not observed in mixtures designed to generate them, even at ~60°C. The highest observed value of \( J(119\text{Sn}–1\text{H}) = 136 \text{ Hz} \), appears to represent a cutoff point which both the complexes are unstable.

Insofar as the electron density on the metal can be quantified, the relationship between this parameter and \( J(119\text{Sn}–1\text{H}) \) appears to be approximately linear (or show only slight curvature), with \( J(119\text{Sn}–1\text{H}) \) increasing as the electron density on rhodium increases. From here, knowing the stability limit of 8 (\( \Delta H \) possibly 10–30 kJ mol⁻¹), the value \( \Delta H \) (~96 kJ mol⁻¹) for 6 and the high stability of 5 (\( \Delta H \) possibly 300–400 kJ mol⁻¹) and also the values of \( J(119\text{Sn}–1\text{H}) \) for these compounds (136, 106 and 29 Hz, respectively), it is not a large step to the following proposal: that \( J(119\text{Sn}–1\text{H}) \) varies as an inverse (at this stage it can only be said that may be approximately linear) function of the dissociation enthalpy, for compounds 5–8. Work still needs to be done to establish more precisely the \( J(119\text{Sn}–1\text{H})/\Delta H \) relationship, but clearly, in principle, it has predictive value. There are, as yet, no grounds for believing that the results can be generalized to a wider variety of types of complex than 5–8. For complexes such as \([\text{Cr}(\text{CH}_3\text{CO})_2\text{Me}](\text{H})\text{SnPh}_2\) and \([\text{Mn}(\text{MeCp})(\text{CO})_2\text{H}]\text{SnPh}_2\) and \([\text{Fe}(\text{CO})_2(\text{cyclopentane})]\), the magnitude of \( J(119\text{Sn}–1\text{H}) \) is 332 and 270 Hz, respectively, this is quite clear.

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2. Jones WD and Feher F.J. (1984). The mechanism and thermodynamics of alkane and arene–carbon–hydrogen bond activation in (C₆H₅)_2R/P(Me)₃/R (R, H, CO, Me, H, NMe) and the magnitude of \( J(197\text{Sn}–1\text{H}) \). Unfortunately, no single comprehensive scale exists by which the nucleophilicities of ligands X and L can be compared. However, when the data are plotted as graphs with NMR parameters on both axes, the electron-donating/withdrawing/nucleophilicity dimension emerges of its own accord. This can be seen in Fig. 1, where a plot of \( J(119\text{Sn}–1\text{H}) \) vs \( \delta(197\text{Sn}) \), for complexes with X = NCBPh₃ and NCO, is approximately linear (except for the uppermost portion) with \( J(119\text{Sn}–1\text{H}) \) increasing and \( \delta(197\text{Sn}) \) decreasing as the complexes become increasingly electron-rich. The plot shown in Fig. 1, when extrapolated, passes not far from the data point for 5 (\( J = 29 \text{ Hz} \)).

![Fig. 1. Plot of \( J(119\text{Sn}–1\text{H}) \) vs \( \delta(197\text{Sn}) \) for complexes 7 and 8. Data obtained from solutions in dichloromethane at ~60°C.](image)

22. Schubert U., Müller J. and Alt H.G. (1987). Hydrido silyl Complexes 9. Cr, H, Si three-center bonding in \([\text{C}_6\text{H}_4\text{CO})_2\text{C}_5\text{H}_4\text{SnPh}_3\), Organometallics 6, 469–472.