Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Structure and bonding in cationic olefin complexes of copper(I) by NMR

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(Received June 12th, 1972)

The NMR spectra of various olefins exhibit apparently random up- or downfield shifts upon coordination with Cu^I. We have found that these changes in chemical shift depend on the structures of the olefin–Cu^I complexes[1] and are correlated by the Dewar–Chatt–Duncanson model of the olefin–metal bond[2]. Up- or downfield shifts can, in turn, be used to evaluate the relative contributions of the synergistic σ and π components to the bonding of various mono- and polyolefinic ligands with metals.

The NMR spectra of olefin-containing solutions varies with Cu^I concentration, but every spectrum contains only a single absorption due to a particular type of proton. These features can be understood in terms of rapid exchange between several different species in equilibrium with one another[3-4]. In some cases, $\Delta\delta_{obs}$, the change in chemical shift of a particular type of proton as Cu^I is added, varies linearly with the ratio of Cu^I/olefin. In these cases we presume the formation of a single complexed species with a large formation constant, and the chemical shifts of protons in the complex can be readily determined★. Previously we reported[1] the isolation and characterization of the olefin–Cu^I trifluoromethanesulfonate complexes (III), (IV), (V), (VI) and (X) shown in Fig. 1, and the crystal structures of which are pending.

Inspection of the $\Delta\delta_{obs}$ for complexes (I)–(X) reveals an unusual dichotomy between vinyl proton shifts in mono- and polydentate ligands. Thus, these shifts are *negative* for monodentate complexes (I), (V)–(VIII), and (IX) while *positive* for polydentate complexes (II), (III), (IV), and (X). We propose that this dichotomy arises from variations in the nature of the metal–olefin bond, which can be generally described as composed of σ and π components[2,6]. The σ component involves overlapping of the occupied bonding π orbital of the olefin with a vacant σ-type metal orbital. The π(backbonding) component involves overlapping of the vacant antibonding π^* orbital of the olefin with a filled metal

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★ For the formation of a single complex $[(\text{metal})_m(\text{olefin})_n]$ with a large formation constant K, a plot of $\Delta\delta_{obs}$ against the concentration ratio [metal]/[olefin] gives a straight line with a slope $n/m\ (\delta_1-\delta_0)$[5]. δ_0 and δ_1 represent the chemical shifts for free and complexed olefin. $\Delta\delta_{obs}$ is positive if the resonance of the complex occurs to low field of the free olefin.

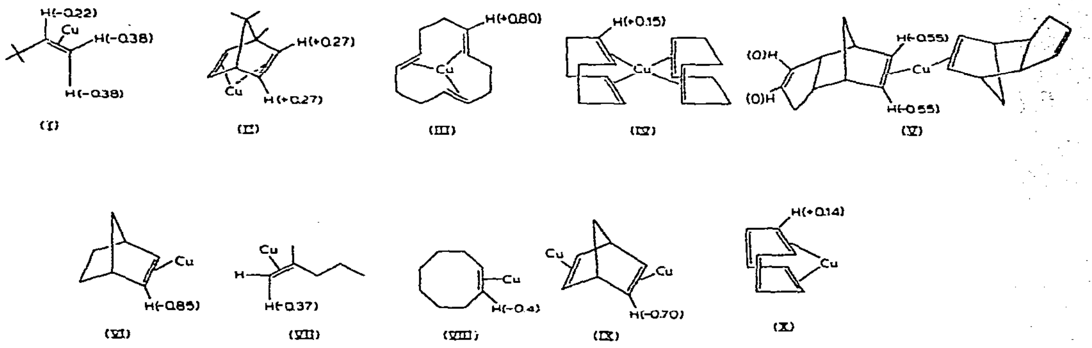

Fig.1. Proposed structures of CuOTf–olefin complexes in solution and the observed changes in the chemical shifts ($\Delta\delta_{obs}$) of the vinyl protons on complexation. For convenience the anion is omitted in these structures.

d orbital. Since the magnetic shielding of the vinyl protons in olefins is directly proportional to π electron density at the carbon[4], the relative contributions of σ and π bonding in a particular metal olefin complex should be reflected in the net shielding (or deshielding) of the vinyl protons accompanying complexation by the metal[7]. Thus, electron donation by σ-bonding results in deshielding, and π-back bonding results in shielding of the vinyl protons upon complexation[4].

Olefin π complexation for most transition metals results in net shielding of vinyl protons[8] indicating a predominance of the π component. The olefin complexes of Ag^I which exhibit net deshielding of the vinyl protons, constitute a glaring exception to this rule and indicate a predominance of the σ component[7]. The behavior of the Cu^I complexes is borderline and corresponds to a greater contribution from the π component. The unique dichotomy of vinyl proton shifts upon olefin complexation with Cu^I can be understood as the result of two factors. First, the σ component increases relative to the π component as the number of double bonds coordinated to the metal ion increases. Second, the σ component is subject to a *trans* effect which diminishes its magnitude. The first generalization accounts for the net shielding in complexes, (I), (VI)–(VIII), and (IX) in which a single double bond is coordinated to each metal atom, and the net deshielding in complexes (II)–(IV), and (X) in which more than one double bond is coordinated to each metal atom★. The second rule accounts for the net shielding in complex (V) in which the presence of two double bonds on the metal is overbalanced by the *trans* effect.

Further support for this model is provided by a consideration of the relative magnitudes of $\Delta\delta_{obs}$ for the α and β vinyl protons of related Cu^I, Ag^I and Au^I complexes (I), (XI), and (XII), respectively. In these complexes, the shielding by the π-component of the metal–olefin bond, should follow the order ($Cu^I > Au^I > Ag^I$) that is expected from the trend in the ionization potentials of these ions

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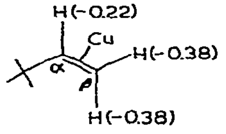
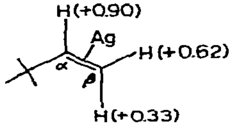
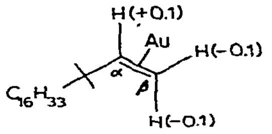
★ The steric hindrance due to methyl substituents in bornadiene would be expected to inhibit *exo*-complexation[9] thus favoring the *endo*-complexed chelate structure (II).



(I)



(XI)



(XII)

[$\mathrm{Cu^{I}}$(20.29 eV), $\mathrm{Au^{I}}$(20.50 eV),$\mathrm{Ag^{I}}$(21.49 eV)] [10], which reflect the ease with which *d*-electrons can be promoted into the valency shell. The greater deshielding of the α compared to the β vinyl protons of (XI) has been attributed to unsymmetrical positioning★ of the silver ion with respect to the trigonal carbon atoms[4]. $\mathrm{Ag^{I}}$ is pictured as being closer to the terminal carbon resulting in more effective π donation ("reshielding") and greater electron density at the less highly substituted carbon atom. While the net change in vinyl proton chemical shifts in (I) is opposite that in (XI), the greater shielding of the proton at the terminal compared to the substituted trigonal carbon atom of (I) is wholly consistent with the same unsymmetrical electron density distribution as in (XI). Gold(I) complexation of terminal olefins[12] such as (XII), results in shielding of the α -protons and deshielding of the β-protons, which can also be understood in terms of a similar variation in the nature of the metal—olefin bond. Preliminary ^{13}C NMR studies also support this view★★.

ACKNOWLEDGEMENT

We wish to thank the National Science Foundation for generous financial support of the work and a referee for assistance in clarifying the presentation.

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★ Unsymmetrical orientation of the metal about the C=C bond has also been crystallographically shown in the $\mathrm{Pd^{II}}$—styrene complex[11].

★★ Other explanations for the chemical shifts of vinyl protons upon complexation to metals have been presented,[5a,13], but these models cannot readily account for the net deshielding observed with $\mathrm{Ag^{I}}$ and $\mathrm{Cu^{I}}$.

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