Journal of Organometallic Chemistry, 425 (1992) 189–200
Elsevier Sequoia S.A., Lausanne
JOM 22327

Ligand-stabilized copper(I) hexafluoroacetylacetonate complexes: NMR spectroscopy and the nature of the copper–alkene bond

Thomas H. Baum *, Carl E. Larson and Gregory May
IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099 (USA)

(Received June 5, 1991; in revised form September 5, 1991)

Abstract

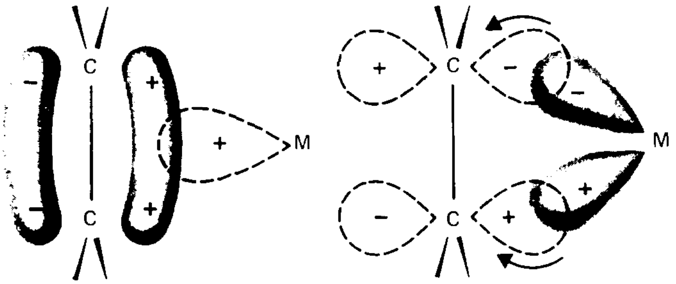
Ligand-stabilized copper(I) hexafluoroacetylacetonate complexes display varying degrees of stability to oxidation and thermal decomposition. In an effort to understand the nature of the copper–alkene bond in these complexes better, ^{1}H and ^{13}C nuclear magnetic resonance spectra were obtained and compared to the spectra of the free alkene. In accord with Dewar–Chatt–Duncanson theory, the extent of π and σ bonding contributions can be qualitatively determined by the observed chemical shift changes upon complexation of the alkene to the copper(I) center.

Introduction

Copper is widely used in the microelectronics industry owing to its low resistivity and reasonable cost. Research into precursors for the chemical vapor deposition of copper films is being actively pursued. The scarcity of stable copper(0) complexes forces one to investigate the diverse chemistry of copper in its higher oxidation states; both the first (d^{10}) and second (d^{9}) oxidation states are useful for forming stable complexes. The first oxidation state has a preferred coordination number of 4 and complexes are often isolated as dimers, as in the case of copper(I) acetate [1], or as tetramers as in the case of copper(I) trimethylsilylmethane [2] and copper(I) pentafluorophenyl [3]. The ability to synthesize discrete, monomeric copper(I) complexes often requires stabilizing ligands (i.e. phosphines) that can π back-bond to the metal center [4]. Monomeric copper complexes are desirable as precursors for copper deposition because they exhibit higher ambient partial pressures than their dimeric or tetrameric counterparts. A wide variety of copper(I) complexes have been synthesized and stabilized by both organic and inorganic ligands [5].

The chemical vapor deposition of high-purity copper films has been demonstrated from a general class of copper(I) β-diketonate complexes [6–8]. The chemical and physical properties of these copper complexes are directly related to the identity of the ligands used to stabilize the copper(I) species [8]. The nature of

0022-328X/92/$05.00 © 1992 – Elsevier Sequoia S.A. All rights reserved



Donation from filled π orbitals to vacant metal orbital

Back-bonding from filled metal orbital to acceptor π^* orbitals

Fig. 1. Schematic representation of alkene-metal bonding as given by Dewar–Chatt–Duncanson theory. σ bonding (left) and π bonding (right) are depicted separately, but normally occur simultaneously upon complexation.

the metal-alkene interaction is often determined by the stabilizing alkene, its geometry, torsional strain and chemical substitution, as well as the ancillary ligands bound to the copper center. The metal–alkene bond features both π and σ overlap between the alkene and the metal center.

Dewar–Chatt–Duncanson (DCD) theory provides an empirical model for metal-alkene bonding [9] which is based upon orbital symmetry rules and the Pauling electroneutrality principle [10]. The σ-bond results from electronic overlap of the occupied alkene π orbitals with the vacant σ (4*s*) orbitals of the metal center (Fig. 1, left side), while the π bond results from electronic overlap of the occupied metal $d\pi$ (i.e. d_{xy} or d_{xz}) orbitals with the vacant antibonding (π^*) orbitals of the alkene ligand (Fig. 1, right side) [9]. In some complexes, the nature of the metal-alkene interaction may be dominated by either the π or σ contribution [11]. The relative importance of the two bonding modes depends strongly upon the transition metal and its oxidation state, the identity and substitution of the alkene ligand, and the nature of the ancillary ligands bound to the metal center (*i.e.* perchlorate, triflate, trifluoroacetate or β-diketonate).

Nuclear magnetic resonance (NMR) spectroscopy is a well known technique for determining molecular structures. In the present case, one can determine the ratio of stabilizing ligand to the copper(I) β-diketonate moiety. Further, as has been demonstrated by Salomon and Kochi [11], a comparison of the chemical shifts for the free alkene and the alkene bound to the copper(I) center enables one to estimate the relative contributions of π and σ bonding in the complex. Although "non-bonding metal *d*-orbital effects" were found to dominate ^{13}C chemical shift changes for d^8 alkene-metal complexes [12], these effects should be minimal for copper(I) because of its full d^{10} electronic configuration [11]. Using NMR spectroscopy in this fashion, Salomon and Kochi determined that σ-bonding was predominant in 1,5-cyclooctadiene copper(I) trifluoromethanesulfonate (triflate) complex and other related copper(I) triflates [11].

In this paper, NMR spectroscopic data is presented for a series of alkene, diene and tetraene complexes of copper(I) β-diketonate. To understand the nature of the copper-alkene interaction in the stabilized hexafluoroacetylacetonate (hfac) complexes, comparative NMR is used to evaluate the extent of σ and π bonding.

As observed in this study, copper-alkene bonding is dependent upon the unsaturated ligand utilized to stabilize the copper complex as well as the identity of the ancillary ligand.

Experimental

The synthesis of alkene stabilized copper(I) hexafluoroacetylacetonate (hfac) complexes has been described elsewhere [13]. The copper(I) hfac complexes used in this study are denoted by the organic stabilizing ligand. The following ligands were complexed to copper(I) hexafluoroacetylacetonate; cyclooctene (COE), 1-methylcyclooctene (MCOE), 1,5-cyclooctadiene (COD), norbornene (NOR), bicyclo (2.2.1) hepta-2,5-diene (BCH), cycloheptene (CHE), and cyclooctatetraene (COT). All of these ligands were purchased from Aldrich or Wiley Organics and used without further purification. The 1,5-cyclooctadiene complexes of 1,1,1-trifluoroacetylacetonate (COD Cu tfac) and trifluoroacetate (COD Cu tfa) [14] were synthesized by reaction of trifluoroacetylacetone (Aldrich) or trifluoroacetic acid (Aldrich) with excess cuprous oxide (Aldrich) in the presence of an equimolar quantity of 1,5-cyclooctadiene. Attempts to isolate a 1,5-cyclooctadiene complex with copper(I) acetylacetonate, COD Cu acac, via the reaction of potassium acetylacetonate hemihydrate (Alfa) and 1,5-cyclooctadiene copper(I) chloride [15*] were unsuccessful; the complex was found to be thermally unstable under ambient conditions.

All of the copper(I) hfac complexes were recrystallized or purified by column chromatography prior to spectral analysis and dissolved in a deuterated solvent (THF-d_8 or $CDCl_3$) to a concentration of roughly 10^{-2} M. The free alkene ligands were dissolved in the same solvent and to roughly the same concentration. This procedure minimizes spectral shifts associated with concentration effects and enables a realistic comparison of the free alkene to that which is ligated to copper(I). $CDCl_3$ and THF-d_8 were purchased from Aldrich with an isotopic purity of 99%.

The NMR spectroscopic data were obtained on an IBM Instruments AF250 NMR spectrometer operating at 250.13 MHz for ^1H and 62.9 MHz for ^{13}C. Samples were ^2H locked using the solvent resonance for $CDCl_3$ or THF-d_8. For the ^1H spectra, 32 scans over a 20 ppm sweep width were digitized into 32 kword data sets. For the ^{13}C spectra, 512 scans over a sweep width of 250 ppm were digitized into 32 kword data sets. The chemical shift changes were calculated by comparing the chemical shifts of the free alkene to the alkene coordinated to copper(I) after referencing the spectra to the solvent: (a) $CDCl_3$, 7.240 ppm for ^1H or 77.000 (triplet) for ^{13}C; (b) THF-d_8, 1.730 and 3.580 ppm for ^1H and 25.3 and 67.4 ppm for ^{13}C spectra. The chemical shift changes for the alkene protons and alkene carbons ($\Delta\delta$) are reported in Table 1 in ppm. The plus or minus sign denotes downfield (deshielding) or upfield (shielding) shifts, respectively. Several NMR control experiments were performed on COD Cu hfac to examine the equilibrium of complexed and free 1,5-cyclooctadiene in solution. COD Cu hfac (0.1 g, 0.00026 mol) was dissolved in 1.0 ml of $CDCl_3$. Both the ^1H and ^{13}C spectra

---

* Reference number with asterisk indicates a note in the list of references.

Table 1
Experimentally determined chemical shift changes for the alkene protons and carbons by comparing the chemical shifts [a] of the free alkene and the alkene coordinated to copper(I) from the ^{1}H and ^{13}C spectra

Complex	$\Delta\delta$ ^{13}C	$\Delta\delta$ ^{1}H
COD Cu hfac	−13.45	−0.02
COD Cu tfac	−14.29	−0.18
COD Cu tfa	−12.92	+0.02
BCH Cu hfac [b]	−13.00	−0.35
COT Cu hfac	−8.14	+0.02
COT (Cu hfac)^2	−16.32	+0.02
NOR Cu hfac	−29.04	−0.74
CHE Cu hfac	NA [c]	−0.34
COE Cu hfac	−18.11	−0.48
MCOE Cu hfac	−13.03 −14.63	−0.26

[a] The chemical shift changes are in ppm after referencing to the residual protons in $CDCl_3$ (7.240 ppm) or carbon signal (triplet) centered at 77.000 ppm. A negative sign indicates an upfield (shielded) shift and a positive sign indicates a downfield shift (deshielded). [b] The NMR data were obtained in THF-d_8 solvent [22]. [c] NA, the data were not available for the ^{13}C spectrum of this complex as a result of decomposition during the analysis.

of COD Cu(hfac) were taken every 20° from −60°C (213 K) up to 0°C (273 K) and compared to the ambient spectra. The variable temperature experiment was used to examine the extent of diene dissociation in solution and the potential for chemical shift changes on the NMR time scale as a result of this equilibrium. No spectral shifts were observed as a function of temperature, although some line broadening was noted in the proton spectra.

Results and discussion

The L_xCu(hfac) complexes are easily synthesized in a single step and in high yield as was previously reported [13]. Spectroscopic data were originally obtained to confirm the expected ratio of the alkene to β-diketonate ligand in the copper(I) complexes. A comparison of spectral data for the alkene copper(I) complexes and the free alkene ligand displayed discrete spectral differences; relative changes in the chemical shifts ($\Delta\delta$) have been observed for both ^{1}H (Figs. 2 and 4) and ^{13}C (Figs. 3 and 5) NMR spectra. Chemical shift changes were reported for alkene copper(I) triflates [11]. Since the multiple bond order decreases upon metal coordination, vibrational spectroscopy can provide useful information with respect to the metal–alkene bond. For example, the alkene stretch (C=C) has been observed to shift to lower frequencies in the infrared [11b] and Raman spectra [16]. The alkene stabilized copper(I) β-diketonate complexes were examined with respect to Dewar–Chatt–Duncanson theory of metal–alkene bonding and the observed NMR chemical shift changes. Further, the effect of changing the ancillary ligand (i.e. β-diketonate) was also examined for a series of 1,5-cyclooctadiene copper(I) complexes.

Proton chemical shifts are determined primarily by local diamagnetic effects and neighboring group anisotropy [17]. Thus, chemical shift changes in the proton

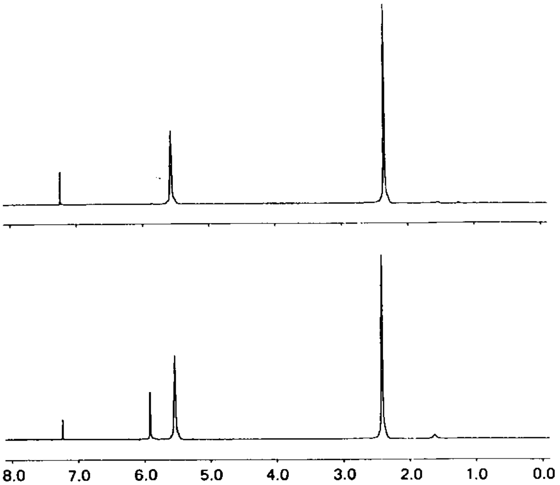


Fig. 2. ^1H NMR spectra for 1,5-cyclooctadiene (top) and 1,5-cyclooctadiene copper(I) hfac complex (bottom) in $CDCl_3$.

spectra are indicative of the electronic environment of the olefinic protons; a decrease in electron density at the alkene due to σ bonding, will cause a net deshielding (downfield) of the alkene protons. Alternatively, π bonding will increase the electron density at the alkene and result in net shielding (upfield) of the alkene protons. Shielding is observed upon examination of the chemical shift changes for BCH, NOR (Fig. 4), CHE, COE and MCOE Cu hfac complexes (Table 1). Similar proton shielding was observed for Cu^1 triflate complexes of NOR, COE and other alkene ligands [11].

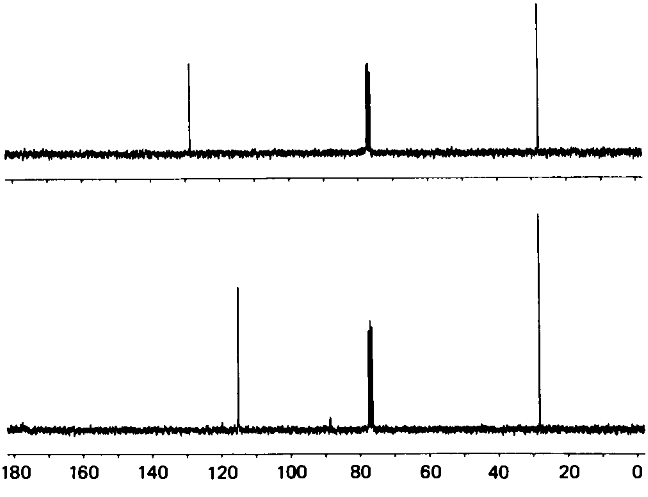


Fig. 3. ^{13}C NMR spectra for 1,5-cyclooctadiene (top) and 1,5-cyclooctadiene copper(I) hfac complex (bottom) in $CDCl_3$. Weak resonances for the hexafluoroacetylacetonate carbons are observed at 88.680 (methine, singlet), 117.757 (CF_3, broad quartet $J = 4.533$) and 177.412 (C=O, quartet $J = 0.554$) ppm (see Fig. 7).

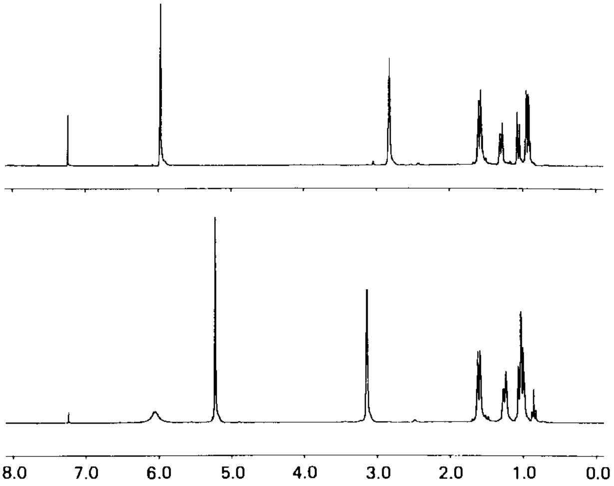


Fig. 4. ^{1}H NMR spectra for norbornylene (top) and norbornylene copper(I) hfac complex (bottom) in $CDCl_3$.

In general, the local paramagnetic contribution (σ_p) is primarily responsible for chemical shift changes in the carbon spectra [18]. The local paramagnetic contribution is influenced by perturbations in the electron density, the multiple bond order and/or a change in the average electronic excitation energy [19]. After considering these effects in the context of DCD theory, the chemical shift changes associated with perturbations of the alkene carbon atoms [11] for both π and σ bonding to copper(I) are given in Table 2. As is evident from Table 2, deshielding of the alkene carbons will occur for σ bonding only as a result of decreased electron density. Deshielding, however, may be negated by shielding effects as a result of a decreased bond order and/or an increase in the average excitation energy of the

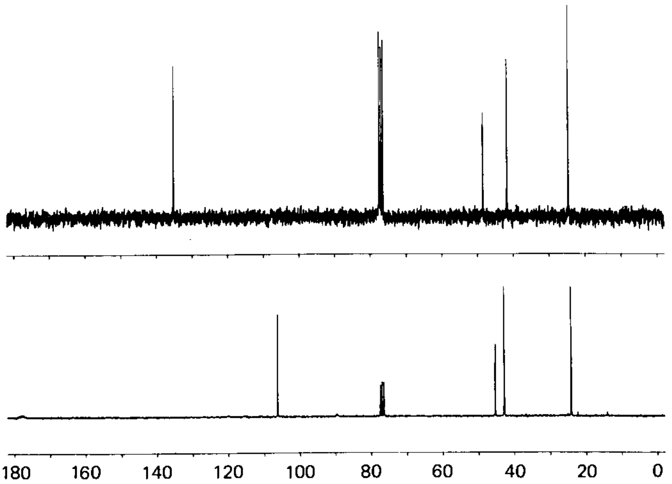


Fig. 5. ^{13}C NMR spectra for nobornylene (top) and norbornylene copper(I) hfac complex (bottom) in $CDCl_3$. Weak resonances for the hexafluoroacetylacetonate carbons are observed at 88.680 (methine, singlet), 117.757 (CF_3, broad quartet $J = 4.533$) and 177.412 (C=O, quartet $J = 0.554$ ppm (see Fig. 7).

Table 2

	$\Delta\delta$
Perturbation due to σ bonding	
Decrease electron density	Deshielding
Decrease multiple bond order	Shielding
Increase energy gap (ΔE)	Shielding
Perturbation due to π bonding	
Increase electron density	Shielding
Decrease multiple bond order	Shielding
Increase energy gap (ΔE)	Shielding

alkene. Thus, in most cases, a net upfield shift (shielding) will be observed for alkene carbons upon coordination to copper(I). Shielding was observed for each copper(I) complex examined in this study (Table 1) and also for the previously reported alkene copper(I) triflate complexes [11]. Further, an evaluation of both the multiple bond order and the excited state energies in the complexes is not easily accomplished. Normally the bond order decreases upon coordination to the metal center; a lowering of the C=C bond stretch energy [11b] is observed in the IR spectrum upon complexation. In our case, the IR absorbances from the β-diketonate ligand are quite intense and occur in the same spectral region (1700–1450 cm^{-1}). Therefore, no information on the C=C bond order is experimentally available. In the copper-alkene complexes, the average excitation energy increases due to orbital mixing of the π and π^* states with the metal orbitals of the correct symmetry (b_2 and a_1, respectively) [20]. The HOMO-LUMO electronic splitting will determine the average excitation energy value (ΔE) of the copper complex and thereby influence the ^{13}C chemical shift of the coordinated alkene carbons. Because estimating the HOMO-LUMO transition energy is not easy [21*], the copper–alkene bond can be evaluated only in a qualitative sense based upon the NMR spectral shifts.

The energetics of the π and π^* states of the alkene are important for metal-ligand bonding because these states will mix with the metal electronic orbitals (Fig. 1) to define the molecular orbitals of the complex. The overlap of the alkene orbitals with the metal orbitals will depend upon the alkene, chemical substitution of the alkene (i.e. electron withdrawing or donating substituents) and the energies of the alkene as a result of ring strain or trans conformation. For alkenes with electron donating substituents (*i.e.* alkyls), both the π and π^* states increase in energy [20] and the σ bonding component increases relative to bonding in the non-alkylated analogue. Nevertheless, π bonding still dominates the metal-alkene interaction. This effect can be observed by comparing COE and MCOE Cu hfac complexes. Both alkene protons and carbons in MCOE are deshielded relative to the chemical shifts for COE (Table 1), but π bonding is still dominant based upon the proton shift changes. For electron withdrawing substituents on the alkene (*i.e.* halogen or CF_3), the opposite is expected and the π bonding component should increase while the σ bonding component decreases.

In cases where the orbital overlap of the alkene and the metal are large, both π and σ bond contributions may be roughly equal. Thus, deshielding of the alkene protons due to decreased electron density (σ bonding) can be negated by shielding

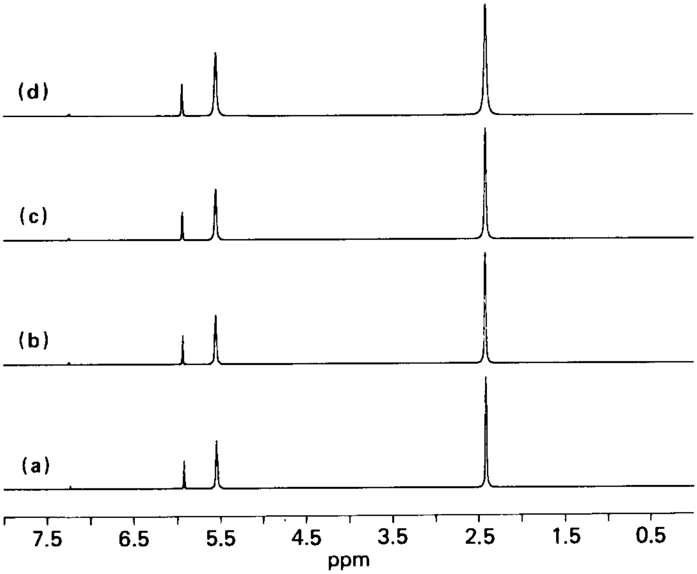


Fig. 6. Variable temperature ^1H spectra of COD Cu (hfac) in $CDCl_3$: (a) 0°C; (b) −20°C; (c) −40°C; (d) −60°C. No spectral shifts were observed with decreasing temperature and indicates that the equilibrium for ligand dissociation in COD Cu (hfac) in solution is relatively small. Some line broadening is observed at low temperature as would be expected.

of the alkene protons due to increased electron density (π back-bonding). In such a case, a small or minimal chemical shift change ($\Delta\delta$) would be observed for the alkene protons, as is observed for COD Cu hfac (Fig. 2), COT Cu hfac and COD Cu tfa. (In the latter complex, however, the σ bonding component is slightly increased relative to COD Cu hfac based upon the deshielding observed in both the ^1H and ^{13}C spectra.)

An equilibrium between the complexed and free organic ligands could be responsible for some of the observed chemical shifts. To examine this, a variable temperature NMR experiment was conducted on COD Cu hfac. No chemical shift changes were noted with decreasing temperature in either the ^1H or ^{13}C spectra (Figs. 6 and 7, respectively). This indicates that the equilibrium constant for dissociation of the COD complex is small in solution. Thus, even at low temperature (−60°C) no chemical shifts are a result of dissociation of the COD ligand (or hfac) ligand on the NMR time scale. Although the potential for a COD_2 Cu hfac complex does exist, a recently reported X-ray crystal structure [22] found this complex to be a stable complex with one COD ligand per Cu hfac moiety. Therefore, the reported chemical shifts for the COD copper complex are a result of the copper(I) interaction upon complexation and not a result of dissociation or formation of a separate species. It should be noted that the equilibrium constant could vary with the organic ligand used to stabilize the copper(I) complex and this requires further study.

In the case where the alkene is strained by its presence in a ring system or is configured in a *trans* conformation, the energies of both the π and π^* states are lowered. This, in turn, alters the molecular orbital energies of the copper complex and π bonding should increase. For BCH Cu hfac [23*], the associated ring strain

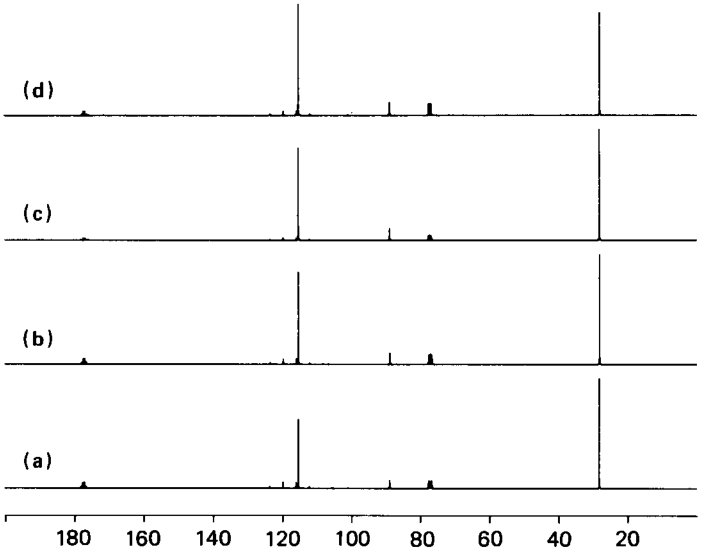


Fig. 7. Variable temperature ^{13}C spectra of COD Cu (hfac) in $CDCl_3$; (a) 0°C; (b) −20°C; (c) −40°C; (d) −60°C. No spectral shifts were observed with decreasing temperature and indicates a relatively small equilibrium for ligand dissociation for COD Cu (hfac) in solution.

of the diene may be responsible for the relatively large shielding observed in the proton spectrum (−0.35 ppm). Although no inequivalence is observed in the alkene protons at room temperature, it is possible that *exo* coordination of one alkene to the copper(I) center results in shielding analogous to that observed for other alkenes in this study. Low-temperature NMR or X-ray crystal structure analysis may provide further information on the exact bonding in this complex and explain the observed proton shielding. Nevertheless, the proton shielding is in sharp contrast to that observed for all the other diene or tetraene Cu hfac complexes in this study (Table 1) and to the analogous Cu^I triflate complexes [11].

For the alkene carbons, an upfield shift (shielding) is expected, as stated above. The degree of shielding varies with the overall change in the paramagnetic contribution. For example, if deshielding due to decreased electron density (dominant σ bonding) is much larger than the shielding effects due to a decreased bond order and an increased average excitation energy (ΔE), then a large downfield shift should be observed. Alternatively, a small deshielding due to an equal or roughly equal π and σ bonding mode may lead to an upfield shift as a result of shielding from a decreased bond order and an increased average excitation energy. Furthermore, chemical substitution of an alkene will alter the paramagnetic contribution; chemical shift changes are observed for the alkene carbons with alkyl substitution. This effect is evident by comparing MCOE Cu hfac with COE Cu hfac. In this case, the carbon chemical shift displays a smaller upfield shift (decreased shielding), which is indicative of increased σ bonding. (This is also supported by the decreased upfield proton shift in MCOE.) Examination of the carbon chemical shifts in the MCOE complex exemplifies the effect of methyl substitution. The methyl substituted alkene carbon is deshielded with respect to the neighboring non-alkylated alkene carbon, as shown in Table 1.

Since DCD theory is related to electroneutrality, the electron density of the copper center is extremely important for copper-alkene bonding. Low oxidation state metals favor π back-bonding with the alkene as a means of dissipating the high electron density on the metal [12]. Also, decreasing the electron density of the metal center favors σ bonding while simultaneously decreasing the π back-bonding contribution. Since the electron density of the metal center may be altered by the properties of the ancillary ligand, in this case the β-diketone ligand, it is expected that changing the electronic properties of this ligand will directly affect the metal-alkene bonding mode. The ability to alter the β-diketone, for an identical alkene–copper(I) system, enables one to examine the role of the ancillary ligand towards metal-alkene bonding directly. For example, a shift from electron withdrawing substituents (CF_3) to electron donating substituents (CH_3) on the β-diketonate will increase the electron density on the copper(I) center and increased π back-bonding would be expected. Alternatively, increasing the electron withdrawing potential of the ancillary ligand would be expected to lower the electron density of the metal and decrease the π bonding component at the alkene.

The relationship of the ancillary ligand towards metal-alkene bonding was examined using several 1,5-cyclooctadiene copper(I) complexes in which the ancillary ligand was altered. As can be seen in Table 1, the bonding mode shifts from roughly equivalent π and σ bonding in the COD Cu hfac complex to one in which π bonding (upfield shift-shielding of alkene protons) is increased for the COD Cu tfac. Thus, replacing one trifluoromethyl group with a methyl group on the β-diketonate increases the electron density on the metal and results in greater π back-bonding with the diene. Furthermore, upon changing the ancillary ligand from hexafluoroacetylacetonate (hfac) to trifluoroacetate (tfa), which is a stronger acid (greater electron withdrawing potential), a slight downfield shift in the alkene protons is accompanied by deshielding of the alkene carbons. Both of these are indicative of increased σ bonding compared to the 1,5-cyclooctadiene Cu^I β-diketonates.

A survey of the chemical shifts for alkene stabilized copper(I) triflate complexes further supports the importance of the ancillary ligand. It was reported [11a] that σ bonding dominated the metal-alkene bonding mode when 1,5-cyclooctadiene was coordinated to copper(I) triflate. The chemical shift change ($\Delta\delta$ ^1H) between coordinated and free diene was $+0.24$ ppm in the 1:1 complex and clearly indicates a σ bonding preference in this complex. This effect has important implications for alkene stabilized copper(I) complexes. First, it may be possible to improve the orbital overlap of the copper(I) center with various alkenes by altering the electronic properties of the ancillary ligand. As is clearly evident, the σ bonding component increases with the acidity of the ancillary ligand, such that triflate > tfa > hfac > tfac, for COD Cu^I complexes. Secondly, the stability of the 1,5-cyclooctadiene copper(I) complexes, in our hands, was observed to decrease as the π back-bonding component increased. This relationship is supported by the inability to isolate a stable COD Cu acac complex, which is expected to display significant π back-bonding in comparison to both COD Cu hfac and COD Cu tfac.

Conclusions

Nuclear magnetic resonance spectroscopy of a series of ligand stabilized copper(I) complexes is reported; comparison of the free alkene and the alkene bound to the copper(I) center displayed chemical shift changes which are indicative of the copper-alkene bonding mode. Copper(I) hfac complexes stabilized by cycloalkene ligands are found to be dominated by π bonding while in the case of 1,5-cyclooctadiene and cyclooctatetraene the situation is more complex. Apparently, copper-diene bonding displays nearly equal π and σ contributions as evidenced by the small proton spectral shift upon complexation. Alkyl substitution of an alkene can increase both the π and π^* state energies and increase the σ bonding contribution in the complex. Decreased shielding is observed for methyl substituted alkenes when compared to the non-methylated analogues. Changing the ancillary ligand (replacing hfac with tfac) increases the electron density of the copper(I) center and increased π bonding is observed. Alternatively, replacing the hfac with tfa results in greater σ bonding, due to a decrease in electron density of the copper(I) center. Experimental observations indicate that the stability of a series of 1,5-cyclooctadiene copper(I) complexes coincides with the nature of the metal–alkene bond. Complexes in which the alkene displays a high degree of orbital overlap with the metal orbitals exhibit roughly equal σ and π bonding contributions. For the cyclooctadiene copper(I) complexes in which π back-bonding was found to be dominant, these complexes were observed to be less thermally stable.

Acknowledgment

The authors gratefully acknowledge Christopher Moylan for his critical reading of the manuscript.

References and notes

1 T. Ogura, R.D. Mounts and Q. Feranando, J. Am. Chem. Soc., 95 (1973) 949; D.C.K. Lin and J.B. Westmore, Can. J. Chem., 51 (1973) 2999.

2 M.F. Lappert and R. Pearce, J. Chem. Soc., Chem. Commun., (1973) 24; J.A.J. Jarvis, R. Pearce and M.F. Lappert, J. Chem. Soc., Dalton Trans., (1977) 999.

3 W.A. Sheppard, J. Am. Chem. Soc., 92 (1970) 5419; A. Cairncross, W.A. Sheppard and E. Wonchoba, Org. Synth. 59 (1973) 122.

4 M.B. Dines, Inorg. Chem., 11 (1972) 2949; W.A. Anderson, A.J. Carty, G.J. Palenik and G. Schreiber, Can. J. Chem., 49 (1971) 761; A. Miyashita, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jpn., 50 (1977) 1109.

5 F.H. Jardine, Adv. Inorg. Chem. Radiochem., 17 (1975) 114; F.R. Hartley, Chem. Rev., 73 (1973) 163.

6 H.K. Shin, K.M. Chi, M.J. Hampden-Smith, T.T. Kodas, J.D. Farr and M.F. Paffett, Mater. Res. Soc. Symp. Proc., 204 (1990) 416; H.-K. Shin, K.-M. Chi, M.J. Hampden-Smith, T.T. Kodas, J.D. Farr and M.F. Paffett, Adv. Mater., 3 (1991) 246.

7 S.K. Reynolds, C.J. Smart, E. Braren, T.H. Baum, C.E. Larson and P.J. Brock, Appl. Phys. Lett., 59 (1991) 2332.

8 T.H. Baum and C.E. Larson, unpublished results.

9 M.J.S. Dewar, Bull. Chem. Soc. Fr., 18 (1951) C79; J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.

10 R. Mason, Chem. Soc. Rev., 1 (1972) 441.

11 (a) R.G. Salomon and J.K. Kochi, J. Am. Chem. Soc., 95 (1973) 1889; (b) R.G. Salomon and J.K. Kochi, J. Organomet. Chem., 64 (1974) 135; (c) R.G. Salomon and J.K. Kochi, ibid.; 43 (1972) C7.
12 D.G. Cooper, R.P. Hughes and J. Powell, J. Am. Chem. Soc., 94 (1972) 9244.
13 G. Doyle, K.A. Erikson and D. Van Engen, Organometallics, 4 (1985) 830.
14 M.B. Dines, Inorg. Chem., 11 (1972) 2949.
15 The method utilized to synthesize COD Cu Cl was described in Chem. Abstr., 76 (1972) 4017c and relies upon the reduction of $CuCl_2$ in alcoholic solution in the presence of the diene. Alternate synthetic approaches are given by M. Hakansson and S. Jagner, J. Organomet. Chem., 397 (1990) 383 and G.N. Schrauzer and S. Eichler, Chem. Ber., 95 (1962) 260.
16 H. Masuda, M. Munakata and S. Kitagawa, J. Organomet. Chem., 391 (1990) 131; T.J. Leedham, D.B. Powell and J.G.V. Scott, Spectrochim. Acta, 29A (1973) 559.
17 J.M. Sichel and M.A. Whitehead, Theor. Chim. Acta, 5 (1966) 35.
18 M. Karplus and J.A. Pople, J. Chem. Phys., 38 (1963) 2803.
19 J.A. Pople, Mol. Phys., 7 (1963) 301.
20 T.A. Albright, Tetrahedron, 38 (1982) 1339.
21 The HOMO-LUMO excitation may be complicated in the UV-visible spectra by the presence of ligand centered $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ state transitions as well as $d-d$, ligand to metal and metal to ligand charge-transfer states. For molecular orbital treatment of a simple alkene Cu^I system and excited states, see R.H.M. Dudzelaar, R.J.J.A. Timmermanns, A. Mackor and E.J. Baerends, J. Organomet. Chem. 331 (1987) 397.
22 A.W. Maverick, F.R. Fronczek, G. Lai and G.L. Griffin, Presentation 256 at the 201st ACS National Meeting, Atlanta, Georgia, 1991.
23 The BCH Cu hfac complex is believed to be a 1:1 complex based upon the proton integration (4:0.8:2.2:2) of resonances in THF-d_8. No evidence for a 1:2 complex was found in contrast to that reported by Doyle *et al.* [13].