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OLEFIN AND ACETYLENE COMPLEXES OF DIVALENT COPPER

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SUMMARY

Phenylacetylene and a number of olefins react with anhydrous copper bis(hexafluoroacetylacetonate) in organic solvents to form deep green 1/1 five-coordinate adducts. The adducts cannot be isolated, but are studied by UV-visible and NMR spectroscopy.

INTRODUCTION

Although olefin complexes have been reported for most of the transition metals, including copper(I), silver and gold[1], no olefin complexes of copper(II) are known. We have recently shown that the very good Lewis acid copper bis(hexafluoroacetylacetonate), $Cuhfac_2$, forms stable 1/1 adducts with di-tert-butylnitroxide[2] and with tertiary phosphines[3], and we now show that $Cuhfac_2$ also forms very labile complexes with olefins.

RESULTS AND DISCUSSION

Funck and Ortolano[4] have recently reported that formation of the 1/1 adducts $Cuhfac_2 \cdot L$ ($L = H_2O$, ethanol, pyridine) causes systematic changes in the *d–d* transition envelope in the visible region of the spectrum, the band at 18,000 cm^{-1} ($\varepsilon = 24$) in the spectrum of $Cuhfac_2$ disappearing so that the colours change from blue-green to green. In addition, in all three cases the extinction coefficients of the *d–d* bands at lower energies increase. Similar behaviour is observed for di-tert-butylnitroxide[2] and tertiary phosphines[3].

On adding phenylacetylene and the olefins listed in Table 1 to solutions of $Cuhfac_2$ (4.0×10^{-1} *M*) in chloroform, the solutions in all cases turned bright green, implying coordination of the hydrocarbons to the copper. The changes in the visible spectrum as the olefin/copper ratio increased is illustrated in Fig. 1 for cyclohexene. As can be seen, the band at 18,000 cm^{-1} decreases in intensity while that at about 15,000 cm^{-1} increases. The presence of a reasonably good isosbestic point shows that only two species were present in solution, and thus the product was presumably the 1/1 adduct, $Cuhfac_2 \cdot$cyclohexene. An equilibrium constant of 1.2 ± 0.3 $l \cdot mole^{-1}$ was calculated using standard procedures[5] and inspection of the spectra shows that formation of the 1/1 adduct was not complete until an olefin/copper ratio of $> 100/1$

TABLE 1

ISOTROPIC SHIFTS AND LINE-WIDTHS IN THE PRESENCE OF 0.4 *M* Cuhfac$_2$

Olefin (1 *M*)	Isotropic shift (Hz)	$\Delta\nu_{\frac{1}{2}}$ (Hz)
Phenylacetylene		
C≡C–H	7	44 (1)[a]
Cyclopentene		
Olefinic H	20	29 (2)
α-CH$_2$[b]	6	23 (5)
β-CH$_2$[c]	2	28 (10)
Cyclohexene		
Olefinic H	15	32 (3)
α-CH$_2$[b]	2	25 (11)
β-CH$_2$[c]	0	22 (10)
1,3-Cyclohexadiene		
Olefinic H	23	41 (3)
CH$_2$	11	25 (3)
1,4-Cyclohexadiene		
Olefinic H	24	41 (2)
CH$_2$	18	22 (3)
Norbornadiene		
Olefinic H	10	24 (4)
α-CH[b]	6	17 (6)
β-CH$_2$[c]	9	21 (4)
Cycloheptatriene		
1-H	10	37 (23)
2-H	16	41 (16)
3-H	11	38 (8)
CH$_2$	11	33 (14)

[a] Figures in parentheses are the line widths in the absence of Cuhfac$_2$. [b] α to the double bond. [c] β to the double bond.

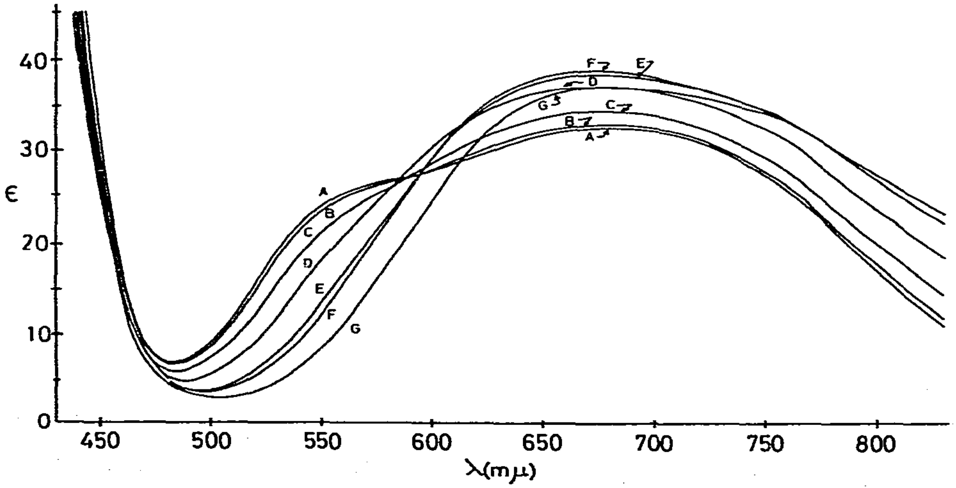


Fig. 1. Visible spectra of Cuhfac$_2$ solutions (4.0×10^{-1} *M*) in the presence of cyclohexene. Olefin: copper ratios: A, 0; B, 1.4; C, 12; D, 50; E, 98; F, 157; G, solution in neat cyclohexene.

was reached. This result can be contrasted with the pyridine case[4], where a ratio of ligand/copper of only 1/1 was required for complete formation of the 1/1 adduct. Thus pyridine, as expected, is a much better donor toward $Cuhfac_2$ than is cyclohexene. The other olefins and phenylacetylene gave similar results.

We also examined the NMR spectra of the $Cuhfac_2$-hydrocarbon solutions in order to gain more information on the mode of bonding. We have previously shown[6,7] that the NMR spectra of solutions of organic ligands in the presence of small amounts of a paramagnetic transition-metal ion can give much information concerning the nature of the metal–ligand interactions. Coordination of an organic ligand to a paramagnetic metal ion can result in delocalization of unpaired electron spin density into the ligand molecular orbitals. The result is broadening and isotropic shifts of the ligand proton resonances, effects which are rapidly attenuated through a saturated molecule and thus are greatest for protons nearest the donor atom(s). Even in the absence of electron spin delocalization, dipolar shifts and broadening would cause the same effects. If exchange between free and coordinated ligand is rapid on the NMR time scale, only one resonance is observed for each proton, the chemical shift of which is related to the mole fraction of the ligand coordinated.

The NMR spectrum of phenylacetylene (1 *M* in $CDCl_3$) is shown in Fig. 2A; chloroform (τ 2.75) and cyclohexane (τ 8.58) were added to serve as inert internal references for both the chemical shifts and the line widths, since some line broadening is expected even in the absence of chemical interactions. Fig. 2B shows the spectrum

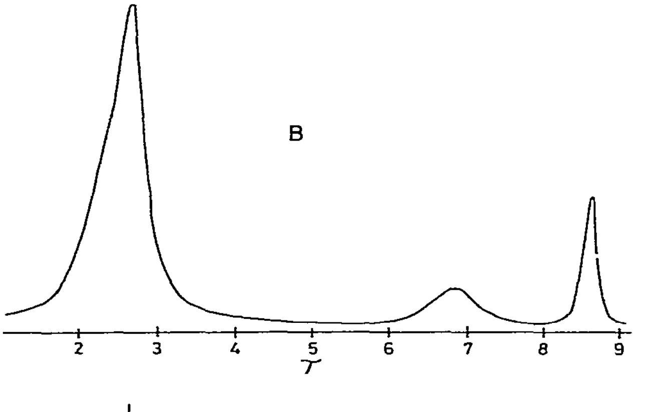


Fig. 2. NMR spectra of 1 *M* solutions of phenylacetylene in the absence (A) and the presence (B) of 0.4 *M* $Cuhfac_2$.

of the same mixture with 0.4 *M* Cuhfac$_2$ added. As can be seen, the acetylenic proton resonance at τ 6.97 shifts downfield about 7 Hz relative to the cyclohexane resonance, and broadens considerably more. The width at half-height, $\Delta\nu_{\frac{1}{2}}$, of the acetylenic proton resonance is about 44 Hz, while that of the cyclohexane resonance is only about 11 Hz.

The spectra of 1 *M* solutions of 1,4-cyclohexadiene in the absence and presence (0.4 *M*) of Cuhfac$_2$ are shown in Figs. 3A and 3B. Again the resonances of the chloroform and cyclohexane are unshifted and broaden about 11 Hz. In addition the olefinic proton resonance at τ 4.37 shifts downfield 24 Hz and broadens considerably ($\Delta\nu_{\frac{1}{2}} \approx 41$ Hz), while the methylene resonance shifts 18 Hz and broadens to a lesser degree ($\Delta\nu_{\frac{1}{2}} \approx 22$ Hz), but still considerably more than the cyclohexane or chloroform. Attempts to isolate olefin complexes by removal of solvent in the cold under reduced pressure yielded only Cuhfac$_2$.

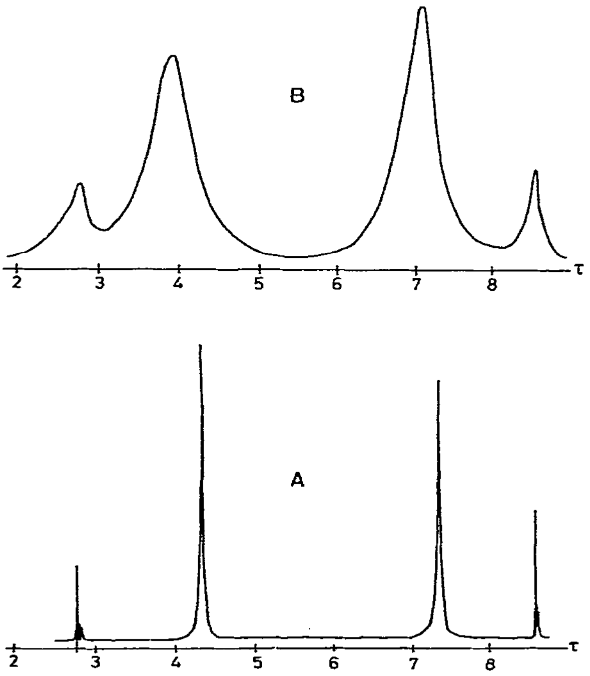
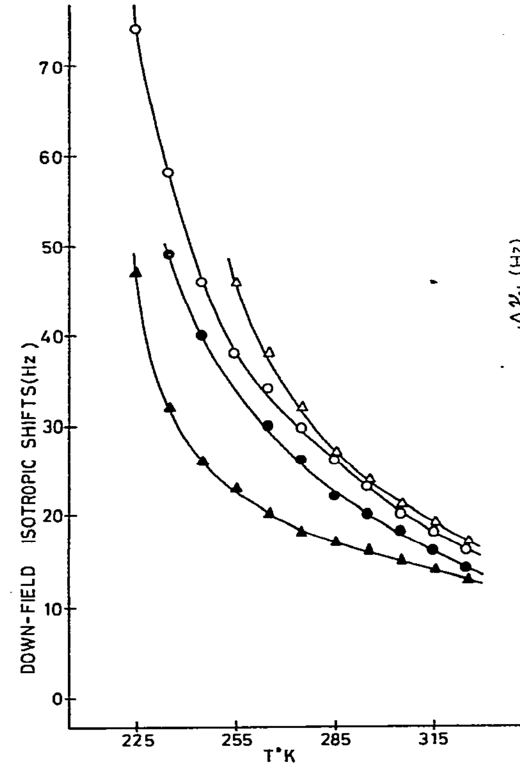


Fig. 3. NMR spectra of 1 *M* solutions of 1,4-cyclohexadiene in the absence (A) and the presence (B) of 0.4 *M* Cuhfac$_2$.

Room temperature isotropic shift and line broadening data for the hydrocarbons studied are listed in Table 1. In most cases, the resonances studied are multiplets in the absence of Cuhfac$_2$ and thus the changes in line-width are somewhat ambiguous. Generally, however, the broadening is greater for the protons nearer the olefin double bond.

The isotropic shifts were measured relative to the literature values for the chemical shifts of the free olefins. As can be seen, the shifts are generally greatest for the olefinic protons, implying coordination in each case. The chemical shifts of each resonance also moved downfield if the Cuhfac$_2$ concentration increased, and thus exchange between free and coordinated ligand must be rapid on the NMR time scale. Attempts were made to distinguish between free and coordinated ligands by lowering the temperature of several olefin/Cuhfac$_2$ mixtures (1 *M* and 0.4 *M*, respectively, in CDCl$_3$) and thus slowing the rate of exchange. Unfortunately, the resonances of the olefinic protons only shifted downfield farther and broadened beyond recognition, as shown in Fig. 4 and Fig. 5. Partenheimer and Drago[8] have shown that the reactions of Cuhfac$_2$ with a number of oxygen- and nitrogen-donor ligands to form the 1/1 adducts are exothermic. Presumably the formation of the olefin adducts is also exothermic, leading to increased formation of the adducts at low temperatures and thus larger shifts and greater broadening.



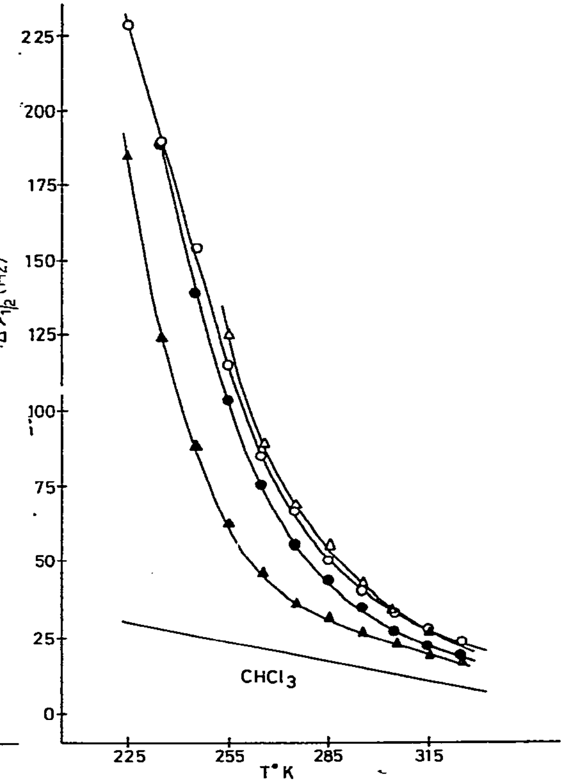


Fig. 4. Temperature dependences of the downfield isotropic shifts of the olefinic proton resonances of 1 *M* cyclohexene (▲), cyclopentene (●), 1,3-cyclohexadiene (○) and 1,4-cyclohexadiene (△) in the presence of 0.4 *M* Cuhfac$_2$.

Fig. 5. Temperature dependences of the line widths of the olefinic proton resonances of 1 *M* cyclohexene (▲), cyclopentene (●), 1,3-cyclohexadiene (○) and 1,4-cyclohexadiene (△) in the presence of 0.4 *M* Cuhfac$_2$.

Formation of the olefin adducts probably involves predominantly a σ interaction between the filled π molecular orbitals on the olefins and empty copper orbitals of the correct symmetry. Back-donation from the copper d_π orbitals into the vacant π

antibonding orbitals is probably unimportant. Cuhfac$_2$ is a much better Lewis acid towards olefins than is Cuacac$_2$, and thus d_π–p_π bonding is likely to be relatively unimportant, as it is for olefin complexes of silver(I)[9].

The shift and line-broadening of the β-methylene resonance of norbornadiene compared to the results for the β-methylene resonance of cyclohexene may suggest that the olefin bonds in an *exo* configuration.

A similar structure has been reported[10] for the complex π-$C_5H_5Mn(CO)_2$-(norbornadiene) and it was suggested[10] that the close approach of the bridging methylene group to the manganese atom might explain the large high-field shift of the resonance of this group in the NMR spectrum. In our case, the broadening and isotropic shift of the methylene resonance would probably be dipolar rather than contact in origin.

The possibility of π interactions between the olefins and the planar hfac ligands seems unlikely, although it cannot be conclusively refuted. Similarly the formation of an adduct such as H(Cuhfac$_2$C≡CPh), or hydrogen bonding between the hfac ligands and the slightly acidic olefinic and acetylenic protons also seem much less likely than the type of interaction postulated above. The changes observed in the visible and NMR spectra are clearly consistent with the formation of a 1/1 adduct of the general formula Cuhfac$_2$·L, with a direct olefin–copper bond.

The NMR spectra of methyl acrylate and vinyl acetate were also studied in the presence of Cuhfac$_2$. In both cases, the methyl resonance broadened and shifted considerably, suggesting oxygen-bonding.

EXPERIMENTAL

Cuhfac$_2$ was prepared by the method of Bertrand and Kaplan[11] and was dried in vacuum over sulphuric acid prior to use. Phenylacetylene and the olefins were purchased from Aldrich Chemical Co.; they were used without further purification because it was found that extensive purification made no difference to the results.

NMR measurements were made with a Bruker HX60 spectrometer with internal TMS lock. Data are for deuterochloroform solutions containing approximately 2% by volume of cyclohexane and $CHCl_3$ as internal references at concentrations 0.4 *M* in Cuhfac$_2$ and 1.0 *M* in organic ligand.

Visible spectra were obtained on a Unicam SP820 spectrometer at concentrations of 4.0×10^{-2} *M*/l in Cuhfac$_2$ and using spectrograde chloroform as solvent.

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