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π-ACCEPTING LIGANDS IN CUPRATE REACTIONS

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Abstract : A Molecular Orbital description of the reductive elimination during alkylation by dialkylcuprates has been used to explain the favourable role of π-accepting ligands such as cyanide or dimethyl maleate.

INTRODUCTION

Ever since GILMAN, JONES and WOODS (1) discovered lithium dimethylcuprate, many other similar copper complexes have been described, many synthetic schemes have employed them, and various studies have endeavoured to assign them a structure. The present study is devoted to finding a theoretical explanation to the higher selectivity exhibited by alkylcyanocuprates compared with dialkylcuprates for the exchange reaction (1):

$$YRCuLi + X\text{-}R' \longrightarrow R\text{-}R' + XYCuLi \qquad (1)$$

rather than the halogen-metal exchange reaction (2):

$$YRCuLi + X\text{-}R' \longrightarrow R\text{-}X + R'YCuLi \qquad (2)$$

STRUCTURE OF CUPRATES

In dialkylcuprates, copper is formally $Cu^{(I)}$, i.e. a d^{10} ion; the d^{10} ions can be tetrahedral as in $(HgI_4)^{2-}$ or linear as in $ZnMe_2$. ORGEL (2) pointed out that the tendency of d^{10} metals to form linear complexes is linked to a small energy difference between the nd and the (n+1)s levels, the metal-ligand bonds being associated with a ds hybridation of the metal. A dimeric structure $(Me_2CuLi)_2$ has often been suggested for dialkylcuprates (3,4) and MO calculations on such a dimer using a modified Extended Hückel Treatment (weighted Hij formula) (5) led to a structure in which each copper atom is linearly linked to two methyl groups (6).

In a linear ligand field (7) the energy levels of the d orbitals are split according to Fig.1. The splitting is large and the $3dz^2$ orbital level is so much raised that hybridization with the 4s orbital is strongly favoured. The d orbital splitting is the more pronounced (and the ds hybridization the more favored) the stronger the field of the surrounding ligands; this is especially so in the case of π-accepting ligands (CO, CN^-, etc...). This was indeed one of the reasons why we first advocated the use of alkylcyanocuprate complexes (8).

Although some discrepancies (essentially due to solvent or salt effects) exist in NMR data on methylcopper species (9), our early observations (Table I) (8c) suggested that the system (MeLi + CuCN) was a new complex MeCuCNLi, quite different from $1/2(Me_2CuLi + (CN)_2CuLi)$, since the chemical shift observed was -1.27 ppm, whereas $Me_2CuLi + (CN)_2CuLi$ without ligand exchange should exhibit the same signal as for Me_2CuLi at -1.05 ppm. This has also been shown in an extensive study (both varying temperature and system (MeLi:CuCN) composition) by LIPSHUTZ and coworkers(10). Not only are the spectra different but also the reactivity (11-17).

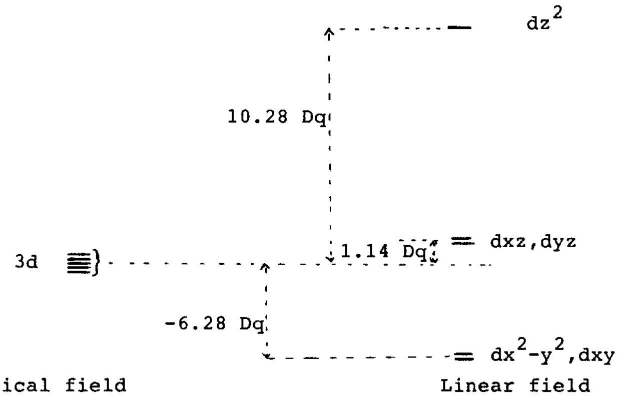


Figure 1 : Splitting of d orbitals in a linear field (7)

Table I

^1H NMR resonance of methyl species (Et_2O, 0°C)

Me species	δ ppm
MeLi	-1.77
Me_2CuLi	-1.05
MeCuCNLi	-1.27

Π-ACCEPTING LIGANDS IN REDUCTIVE ELIMINATION

Cyanide effect

Reaction (1) using bromocamphor as R'-X, is superseded by reaction (2) (8,13b) in the case of Me_2CuLi in ether, whereas it is much less so with MeCuCNLi (see Table II). The proposed mechanism is shown in Scheme 1 (18).

Scheme 1:

$YMeCu^- + R'\text{-}Br \longrightarrow (YMeCuR') + Br^-$ step 1

$(YMeCuR') \longrightarrow Me\text{-}R' + Y\text{-}Cu$ step 2

$(YMeCuR') \longrightarrow Me\text{-}Y + R'\text{-}Cu (\xrightarrow{H_3O^+} R'\text{-}H)$ step 2'

The reductive elimination (step 2) is the key step in the formation of R'-Me.

MO description

Theoretical studies on reductive elimination have shown that reactivity is essentially conditioned by the evolution of b2 orbitals, antisymmetric with regard to the plane of symmetry of the σ bond being made (19).

Important MO's (Fig.2) for YMeCuR', the initial system, are the 1b2 bonding MO between Cu dxy, Me and R' in which electron density is higher on R' and Me, and the corresponding 2b2 antibonding MO in which electron density is mostly on dxy.

In the final system, Y-Cu + R'-Me, those important MO's are the b2 occupied MO, which is Cu dxy only, and the b2 vacant MO, which is the σ* of R'-Me.

The natural monoelectronic correlation occurs between molecular orbitals having their electronic density located mainly on the same atomic orbitals in the initial and in the final systems, thus, first between the 1b2 and σ* (main density on R' and Me) and, second, between 2b2 and dxy (high density on Cu dxy). The "non-crossing rule" then leads to the actual energy evolution of the occupied and the vacant MO's (see Fig.3). So the energy of the occupied MO first increases as the reaction proceeds. ΔE_o, which represents that increase, is the b2 contribution of the electronic rearrangement (electronic density going from R' and Me to Cu dxy) to the activation energy of the process.

Such a diagram has been drawn when Y has no π-type orbitals. If Y is a π-accepting group, as CN^-, the bonding combination of the π*MO on Y with the b2 type MO's lowers the energy of these b2 MO's, the more so, the higher the coefficient of dxy. Thus dxy of Y-Cu is strongly lowered, 2b2 of YCuR'Me is also lowered, whereas 1b2 of YCuR'Me is little stabilized and σ*R-Me remains unaffected. The values of the energy of these b2 orbitals were obtained by Extended Hückel Calculations for $YCuMe_2$, Y=H (no π-bonding) and Y=CN (π-backbonding) and are given on Fig.2. So, as the reaction proceeds, the stabilizing influence of the π-accepting orbital of Y increases in the occupied MO, from the initial to the final system; thus, the new contribution ΔE to the activation energy is lowered, and the yield of R'-Me is improved when Y=CN.

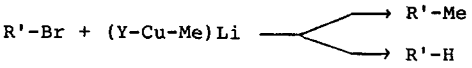
Solvent effects

The effect of π-accepting systems can also be seen in Table II. Among the 8 physicochemical parameters used for describing solvents (20), only εL, i.e. energy of the LUMO, gives a satisfactory correlation with the formation of R'-Me : the lower εL, the higher the ratio R'-Me/R'-H (21). This finding confirms the above mentionned interpretation : any accepting ligand (low εL), by lowering the b2 MO energy, lowers the energy barrier of the reductive elimination.

The improvement of dialkylcuprates reactions on halides and tosylates by HMPA had already been observed (22,23).

Table II (from ref. 13b)

Solvent and ligand effects in reactions of methylcuprates on bromocamphor



R'-Br : Bromocamphor

Y : Me or CN

	Ratio R'-Me/R'-H		
Cosolvent *	Y = Me	Y = CN	EL cosolvent (eV) (20)
Et_2O	4/96	23/77	-2.0 eV
THF	34/66	40/60	-2.7 "
pyridine	39/61	45/55	-9.3 "
HMPA	45/55	54/46	-6.2 "
DMF	76/24	76/24	-8.3 "
DMSO	85/15	88/12	-8.9 "

* ($Cosolvent/Et_2O$ = 1/1)

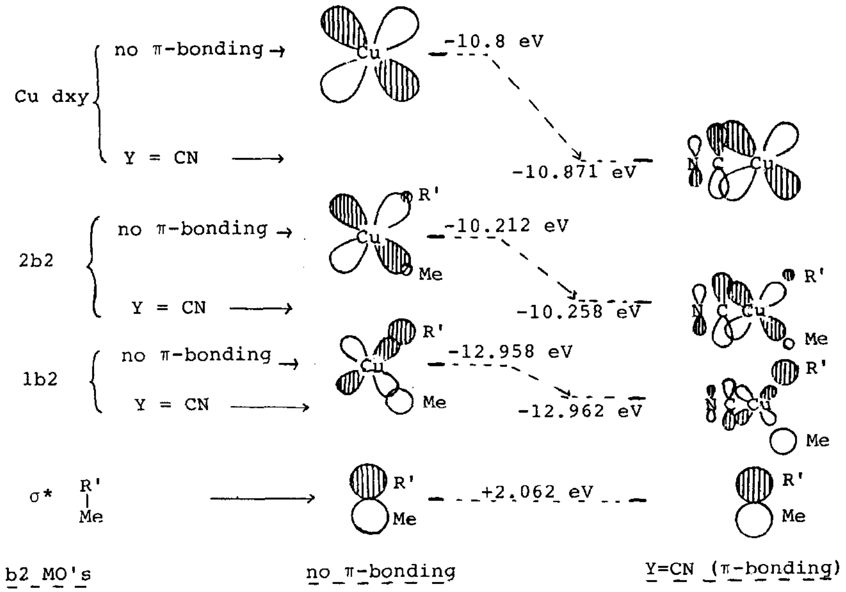


Figure 2: b2 MO's; energy changes through π-bonding

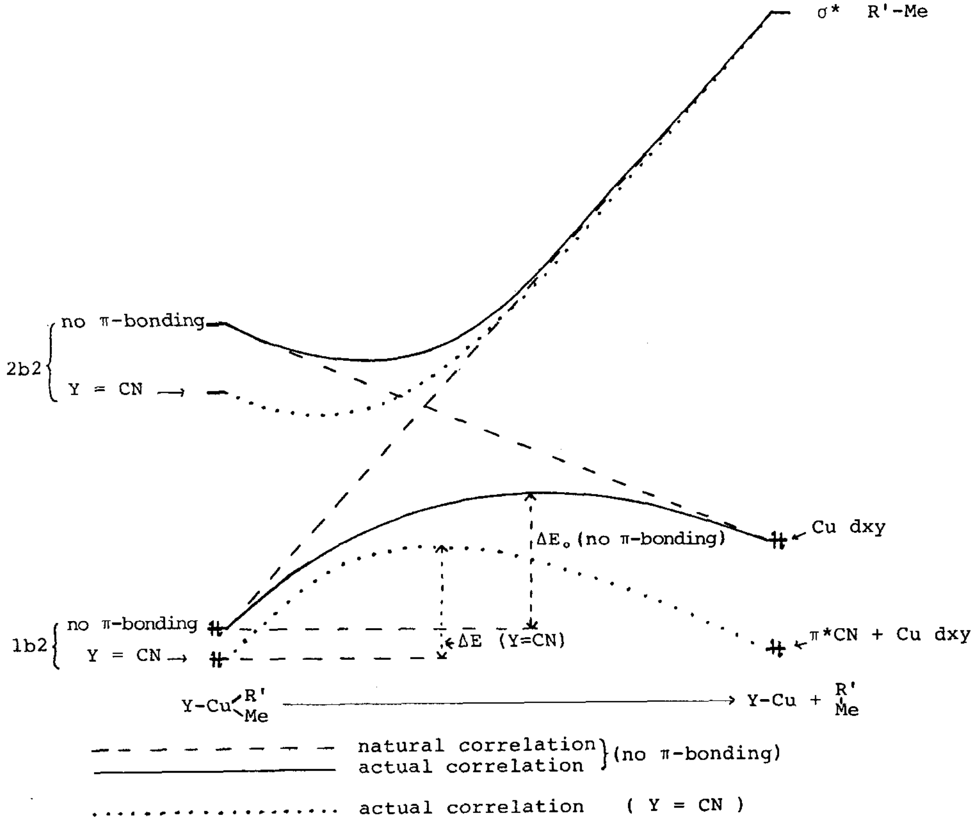


Figure 3: b2 MO's correlation diagram in reductive elimination

Spectator π-accepting ligands

Some of the solvents in Table II may act as π-accepting ligands. It is known that added π-accepting olefins facilitate reductive elimination from dialkylnickel complexes (24) :activation parameters are correlated with the e ALFREY-PRICE parameter of the olefine, which is itself correlated with the π-accepting character of the olefin (25).

The problem in this case arises from the fact that cuprates do react with some π-accepting olefins such as conjugated enones. However unsaturated nitriles could be satisfactory, as suggested by HOUSE (26). As shown in Table III, when Me_2CuLi is reacted with bromocamphor, nitriles indeed improve the ratio R'-Me/R'-H, even though acrylonitrile itself is polymerized in the process. Maleate and fumarate esters, which complex cuprates without leading to addition products (27), also improve the ratio. It can also be seen that trimethyl phosphite brings no improvement, whereas triphenyl phosphite improves the ratio; hindered phosphites are usually regarded as better π-acceptors than unhindered ones (7).

Table III

Reaction of Me_2CuLi with bromocamphor in ether;
Influence of π-accepting ligands upon the alkylation/exchange ratio

Ligand L	R'-Me / R'-H
no ligand	4 / 96
CN a)	55 / 45
PhCN b)	40 / 60
DiMe-Maleate b)	50 / 50
DiMe-Fumarate b)	53 / 47
$P(OMe)_3$ b)	2 / 98
$P(OPh)_3$ b)	41 / 59

a) CN as a cosolvent (CN/Et_2O = 1/1)
b) [L] / [Cu] = 2

CONCLUSION

Alkylation of halides by alkylcuprate complexes is improved by the use of π-accepting ligands, which can be either an ion such as cyanide, or a molecule such as DMSO or dimethylmaleate.

EXPERIMENTAL

All the experimental details are as described in reference 13b. The Extended Hückel Calculations on $H\text{-}CuMe_2$ and $NC\text{-}CuMe_2$ as model compounds for YCuR'Me were performed on a GOULD-UTX32 Calculator at the Centre de Calcul Recherches de l'Université Pierre et Marie Curie; standard parameters for these calculations were taken from Ref.6.

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21) Pyridine does not fit the correlation since, EL being the lowest, the ratio R'-Me/R'-H should be the highest. However pyridine is also a good π-donor and should thus play a dual role (EL = -9.3 eV > EdCu = -11.8 eV >E_{HOMO} = -13.4 eV). It is also known that in the spectrochemical series, pyridine only exerts a medium sized field (7).
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