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Preliminary communication

CARBON—CARBON BOND FORMATION UPON ADDITION OF CYANOGEN TO METAL-COORDINATED β-CARBONYLENOLATO AND β-KETOIMINATO LIGANDS

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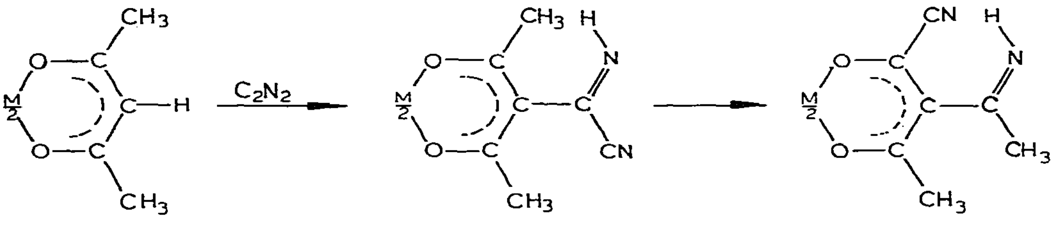
Summary

Addition of C_2N_2 to a variety of metal-coordinated β-carbonylenolato and β-ketoiminato ligands under ambient conditions affords novel compounds bearing cyanoimino-substituted organometallic rings. The key step of this process is the ready formation of a carbon—carbon σ bond upon insertion of C_2N_2 into the C—H methino bond.

The metal-promoted formation of a carbon—carbon σ bond in the framework of an organic substrate is frequently a synthetic objective for organometallic chemists. When this result can be achieved by employing simple "small molecules" and is accompanied by a substantial increase of functionalization in the original organic material, such a process is of special importance.

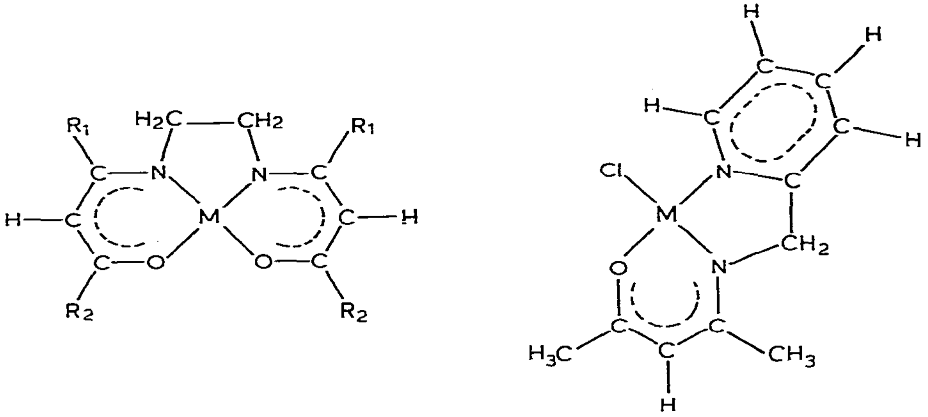
We have found that cyanogen can be readily added to nickel(II) [1] and copper(II) [2] acetylacetonato complexes according to Scheme 1, and have shown that this process is the key-step for the achievement of a new one-pot synthesis of pyrimidinic compounds [2,3] from cyanogen and β-dicarbonylic compounds under ambient conditions.



$M\alpha_2$ $M\beta_2$

SCHEME 1

We have screened the behaviour of C_2N_2 towards a variety of ligands containing "active" hydrogens at carbon atoms and focused our attention on nickel(II), copper(II) and palladium(II) complexes (Scheme 2). The scope of the investigated organometallic substrates and of the relevant results is summarized in Table 1.



SCHEME 2

TABLE 1

PRODUCTS FROM VARIOUS SUBSTRATES

Reactant [a]	Solvent [b]	Product	ν(N—H) [c]	ν(C≡N)	ν(C=N)
$[Cu(eaa)_2]$	A	$[Cu(eaa \cdot C_2N_2)_2]$	3280(m-s)	undetect.	1710(s)
$[Cu(ba)_2]$	A	$[Cu(ba \cdot C_2N_2)_2]$	3330(m-s)	undetect.	1627(m-s)
$[Cu(dbm)_2]$	A	$[Cu(dbm \cdot C_2N_2)_2]$	3253(m-s)	undetect.	1629(m-s)
$[Cu(acac)_2]$	A	$[Cu(acac \cdot C_2N_2)_2]$ [d]	3271(m-s)	2225(w)	1635(s)
$[Cu(tfacac)_2]$	A	none			
$[Ni(eaa)_2]$	A, B	$[Ni(eaa \cdot C_2N_2)_2]$	3270(s)	2230(w)	1705(s)
$[Ni(ba)_2]$	A, B	$[Ni(ba \cdot C_2N_2)_2]$	3270(s)	2240(w)	1645(s)
$[Ni(dbm)_2]$	A, B	$[Ni(dbm \cdot C_2N_2)_2]$	3260(s)	undetect.	1645(s)
$[Cu(enacac_2)]$	A	$[Cu(enacac_2 \cdot (C_2N_2)_2)]$	3280(s)	2220(w)	1650(s)
$[Cu(enba_2)]$	A	$[Cu(enba_2 \cdot (C_2N_2)_2)]$	3315(m-s)	2220(w)	1645(m-s)
$[Cu(pap)Cl]$	A	$[Cu(pap \cdot C_2N_2)Cl]$	3285(s)	2235(w)	1665(s)
$[Ni(pap)Cl]$	A, B	$[Ni(pap \cdot C_2N_2)Cl]\alpha$	3370(m-s)	2235(w)	1665(s)
$[Ni(pap)Cl]$	A, B	$[Ni(pap \cdot C_2N_2)Cl]\beta$	3300(s)	2240(w)	1670(s)
$[Pd(pap)Cl]$	A	none	—	—	—

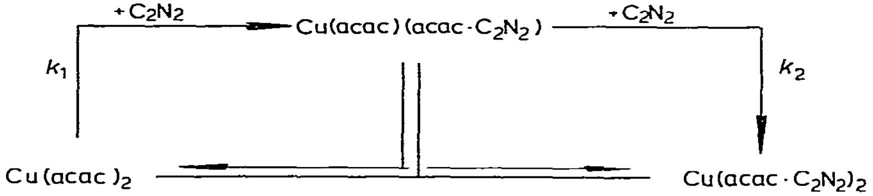
[a] Heaa = ethylacetoacetate; Hba = benzoylacetone; Hdbm = dibenzoylmethane; Htfacac = trifluoroacetylacetone; Henacac$_2$ and Henba$_2$ = Schiff bases from ethylendiamine and acetylacetone and benzoylacetone, respectively; Hpap = Schiff base from α-picolylamine and acetylacetone. [b] A = dichloroethane. B = toluene. [c] Data in cm^{-1}, spectra in nujol mull. [d] Data from ref. 2.

The products were characterized by elemental analysis, by IR, VIS-UV spectra and by a variety of physical methods including X-ray single crystal analysis (for $[Cu(enba_2 \cdot (C_2N_2)_2)]$), mass spectrometry, magnetic measurements, powder Debye spectra, and thermogravimetric analysis.

In contrast with a previous structural attribution [2], $[Cu(acac \cdot C_2N_2)_2]$ is found to be a $M\beta_2$ species (see Scheme 1) (X-ray single crystal analysis) and all the related copper(II) complexes are suggested to display this overall geometry. For all these compounds the extremely weak intensity of the ν(C≡N) band is not surprising in the light of information in the literature [4].

[Cu(enba$_2$·(C$_2$N$_2$)$_2$)] is also found to be a Mβ_2 and we suggest the same geometry for [Cu(enacac$_2$·(C$_2$N$_2$)$_2$)]. [Ni(pap·C$_2$N$_2$)Cl] can be isolated in two different forms, as noted for [Ni(acac·C$_2$N$_2$)$_2$] [1], while [Cu(pap·C$_2$N$_2$)-Cl] could be isolated only as a β species.

The mechanism of the activation of C_2N_2 by the metal complexes is unknown. We find that [Cu(acac)$_2$] reacts with C_2N_2 according to the stoichiometric scheme illustrated in Scheme 3. Steps 1 and 2 are pseudo-first-order in copper(II) and first order in [C_2N_2] (k_1 = 7.4 × 10^{-4} l mol^{-1} s^{-1}; k_2 = 1.7 × 10^{-4} l mol^{-1} s^{-1} at 20°C, in CH_2Cl_2), and the ligand comproportionation constant is 8 ± 2 at 20°C.



SCHEME 3

As to the intimate mechanism, we feel that the metal center plays an important role in the activation of C_2N_2 as shown by the lack of reactivity exhibited by [Cr(acac)$_3$] (in contrast to [Mn(acac)$_3$]), [Pd(acac)$_2$] [2] and [Pd(pap)Cl] (see Table 1).

The failure of [Cu(tfacac)$_2$] to react with C_2N_2 also emphasizes the importance of the features of the coordination sphere in influencing the activation of C_2N_2, and therefore the possibility of achieving C—C σ bond formation. A detailed analysis of the data here will appear later.

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