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VARIATION OF R IN THE ISOCYANIDE SERIES RNC: AS AN EXAMPLE OF THE CONCEPT OF CONTROLLED MODIFICATIONS OF THE PROPERTIES OF LIGANDS FOR ORGANOMETALLIC SYNTHESIS

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ABSTRACT

Basically different behavior inside a homogeneous series of two-electron ligands can be predicted using simple concepts; for example, π-back donation onto RNC: ligands may be dramatically increased with respect to classical alkyl isocyanides by interaction with a carbonyl group in a position α to the nitrogen. Organometallic complexes of Cr(0) bearing such *N*-acylisocyanides ligands have been prepared and studied. From both the electronic and structural points of view, isocyanide ligands allow a wider scope of application in comparison with CO and CS.

The potential of organometallic chemistry to contribute towards fields such as catalysis, stereochemistry and organic synthesis depends strongly on the diversity of the available ligands [1]. Thus, information regarding the coordinating properties of ligands, particularly the evaluation of their electronic effects, is of great importance and can guide the choice of new compounds to be synthesised.

For example, the possible use in homogeneous catalysis of complexes such as η^6-arene $CrL_1L_2L_3$ is related to the ease of reversible decoordination of the arene. Such an ability is largely influenced by the electronic properties of the two-electron ligands L through the metal atom [2]. In this continuation of our study of centro-chiral metals in arene—chromium(0) systems, the lack of another key ligand which is readily exchangeable for CO and yet still maintains high catalytic activity led us to consider modified isocyanide ligands*; in the classical alkyl or aryl isocyanides complexes these ligands exhibit good σ-donating ability but are only moderate π-acceptors [4]. The problem which

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*A solution to the problem might be the good σ-donating and π-accepting CS ligand [1] and indeed this group allows access to enantiomerically stable centro-chiral metal atoms [3]. However, recent study has shown that such chromium complexes are useless as hydrogenation catalysts [2], in sharp contrast to the corresponding *N*-acyl isocyanide derivatives (see below) [5].

arises, therefore, is one of increasing the π-back-donation onto the RNC ligand, while still satisfying the synthetic and catalytic criteria.

While most of the usual experimental methods allow evaluation of the global electronic effects of the ligand, a single theoretical approach permits a complete description of the electronic structure of these moieties, which is useful for experimental chemists. The metal—ligand bonding mode in an organometallic complex may be described starting from a simple scheme of interactions between the metal and ligand frontier molecular orbitals (FMO) (Fig. 1): this FMO formalism [6a] has been described within the framework of a one-electron Hamiltonian (e.g., the so called "one-electron molecular orbital" procedure [6b]).

Perturbation theory predicts that the energetic stabilizations $\delta\sigma, \pi$ are proportional to $S^2\sigma, \pi/\Delta E\sigma, \pi$ with $S\sigma, \pi$ and $E\sigma, \pi$ being respectively the overlapping and the energetic deviations between the interacting molecular orbitals. These molecular orbitals are then the π-HOMO and σ-LUMO orbitals of the metallic fragment on the one hand and the σ-HOMO and π^*-LUMO of the ligand on the other hand.

However, in a homogeneous series of two-electron ligands, the S^2 values retain approximately the same order of magnitude and exhibit negligible variations in comparison with the energetic terms*. Therefore, the importance of the $\delta\sigma$ and $\delta\pi$ stabilizations with respect to the same organometallic moiety is related to the energies of the σ donating and π accepting functions of the ligand. The higher the ligand σ HOMO energy, the better the σ-donating character, while a lowering of the ligand π-LUMO improves the π-acceptor ability. Clearly, these two MO's tend to optimize interactions with the metal orbitals.

An increase in the π-acceptor effect of an isocyanide ligand stabilizes its π^* LUMO antibonding. This should be brought about by interaction with a judiciously selected conjugated system situated in an α position to the nitrogen**. This could also be the case for the carbonyl group. Since the possible existence of *N*-acyl isocyanide ligands has recently been demonstrated [8], we have undertaken a theoretical study of this type of coordination in order to evaluate its potential in organometallic chemistry in relation to the above objective.

The HOMO and LUMO energies of several CNR ligands and, for the sake of comparison, of CO and CS, have been calculated by the ab initio LCAO—MO method by using a double ξ basis of Gaussian type orbitals [9]. The results are shown in Table 1.

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*Overlap integrals calculations between the σ HOMO and π^* LUMO of the studied ligands and either various *3d* functions of Cr, SCF (ref. 12c) or simple gaussian functions of different exponents (0.6 to 0.2), are in agreement with this hypothesis.

**For a favorable interaction the π^* LUMO of an additional π system has to possess an energy near to that of the π_{CN} system of the isocyanide. This is not the case for benzene whose π^* orbitals are more stabilized. This might explain why PhNC: has a behavior close to alkyl isocyanides.

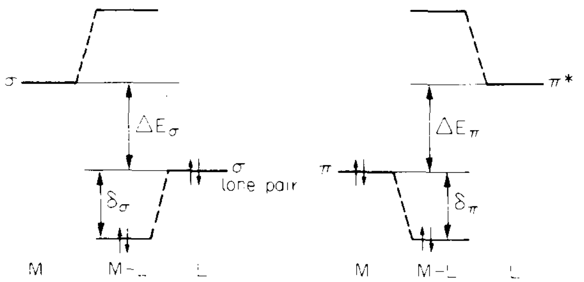

Fig. 1. FMO interaction diagram of a metal—ligand bond.

TABLE 1

Ligands	Geometries	Total energy (a.u.)	σ HOMO energy (a.u.)	π* LUMO energy (a.u.)
CO	c	−112.567 (−112.343)^a	−0.547 (−0.555)^a	0.158 (0.132)^a
CS	c	−434.806	−0.460	0.077
$CNCH_3$	d	−131.734	−0.459	0.212
CNCOH	e	−205.303	−0.480	0.082
CNCOOH	f	−280.039 (−279.505)^a	−0.493 (−0.515)^a	0.086 (0.064)^a
CNCOPh	g	−433.723^a	−0.502^a	0.022^{a,b} 0.114^a
CNCN	h	−184.327	−0.535	0.097

[a] Ab initio calculations carried out using a simple ξ basis. [b] CNCOPh has two π-accepting functions. The lowest in energy, located at 11% on the isocyanide carbon, generally involves a minor interaction with the π-HOMO metal orbital. [c] Interatomic Distances, Spec. Publ. No. 11, The Chemical Society, London, 1958. [d] Ref. 12 except for the ∠CNC angle, which is 180° [e] Ref. 8a for the geometry of the $\mathrm{CN{-}C}^{\nearrow O}_{\searrow}$ moiety, and C—H = 1.12 Å. [f] Ref. 8a for the geometry of the $\mathrm{CN{-}C}^{\nearrow O}_{\searrow}$ moiety, and C—O = 1.40 Å, O—H = 1.03 Å. [g] Ref. 8a. [h] Optimized the MINDO/3 method $(\mathrm{C}\overset{1.16\ \text{Å}}{\text{——}}\mathrm{N}\overset{1.35\ \text{Å}}{\text{——}}\mathrm{C}\overset{1.16\ \text{Å}}{\text{——}}\mathrm{N})$.

The reported molecular structures of isocyanide metal complexes generally exhibit two types of conformations: linear (CNR = 180°) or slightly bent (CNR = 167—171°) [8a, 12, 13] owing to the valence angle CNR. Accordingly, we first evaluated the effect of the isocyanide angular conformation on the electronic structure. Calculations were done for $CNCH_3$ and CNCOH on the two conformations CNR = 180° and 168°. In both cases the results show only weak differences in energy and in the wavefunction distribution. The slight variations encountered are not interpretable in the absence of a complete ab initio optimization of the geometry [14] and the influence of the angular conformation may be neglected. Table 1 displays results corresponding to linear $CNCH_3$ (the most frequently quoted for *N*-alkyl isocyanide complexes) and slightly bent $CNCOR'$ ($R' = H, OH, Ph$). (The only known molecular structure for an acylisocyanide complex exhibits a CNR angle of 168° [8a].)

From Table 1 it is clear that the RNC ligands are all noticeably better σ-donors than CO and that the π-acceptor properties of the isocyanides are greatly dependent on the nature of R. Thus, while CH_3NC: is a poor π-acceptor, R'—C—NC: ($R' = H, OH, Ph$) are better π-acceptors than CO. It is also apparent from the hypothetical ligand CNCOOH that the effect of the hydroxyl oxygen on the stabilization of the π^* LUMO is weak, the major influence being from the π-system of CO in the α position with respect to the nitrogen. The stabilization of the LUMO of the isocyanide function could also be achieved with a suitable π system other than that of CO. We have extended the calculations to the hypothetical ligand CNCN, whose synthesis should be possible. The order for σ donation is $CS \simeq CNCH_3 > CNCOR' > CNCN > CO$ and for -back-bonding $CS \simeq CNCOR' > CNCN > CO > CNCH_3$. It is interesting to note that the $CNCOR'$ ligands appear to occupy an intermediate position between CS and CO. Therefore new fine-tuning organometallic syntheses may be expected.

For example, the above results suggest that the strength of *N*-acylisocyanides ligands, in both the σ and π senses, might allow access to chiral complexes prepared by successive and very selective exchanges of carbonyl groups. Such a study has been undertaken in the arene chromium tricarbonyl series. Upon irradiation of $(PhCO_2CH_3)Cr(CO)_2CNCOPh$ (**1**) [15] in benzene for 1 h in the presence of an excess of $P(OPh)_3$, the chiral complex $(PhCO_2CH_3)Cr(CO)P(OPh)_3CNCOPh$ (**2**) m.p. 77—78°C was formed in 25% yield as the only isolable product. In contrast, the same reaction carried out with $(PhCO_2CH_3)Cr(CO)_2CNCH_3$ (**3**) m.p. 125°C gave rise to $(PhCO_2CH_3)Cr(CO)_2P(OPh)_3$ (**4**) m.p. 85°C, 91% yield. No trace of a chiral product could be detected*. These examples illustrate the dramatic change in behavior met in going from *N*-alkyl isocyanide to *N*-acyl isocyanides when CO is used as the reference ligand. The above experiment can be extended to the preparation of optically active centro-chiral metal atoms. For example, starting from IR $(m\text{-}OCH_3PhCO_2CH_3)Cr(CO)_2CNCOPh$ **5** $(\alpha)^{25}_{D} = +133°$ ($c = 1.09$ g l^{-1}; $CHCl_3$) [16] a mixture of diastereoisomers **6a** and **6b** (scheme 1) was obtained upon irradiation in the presence of $P(OPh)_3$. TLC separation (benzene) yielded **6a** $(\alpha)^{25}_{D} = +132°$ ($c = 1.09$ g l^{-1}, pentane) and **6b**$(\alpha)^{25}_{D} = +115°$ ($c = 1.3$, pentane). These internal diastereoisomers (planar and centro-metalled chiralities), produced in approximately equimolar amounts, are enantiomerically stable in benzene solution.

Another experimental result fits very well with the above calculations.

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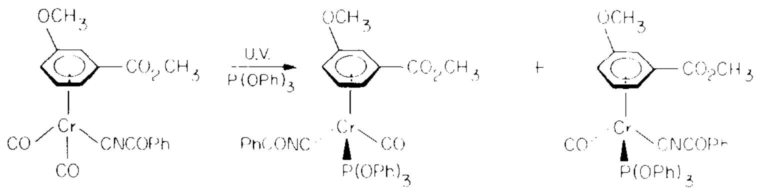
*Interestingly, the IR spectra of **1** and **3** exhibit CO stretching frequencies at, respectively, 1987, 1922 and 1939, 1891 cm^{-1} (A_1 and A_2 modes), in complete agreement with a stronger global ($\sigma + \pi$) electron-accepting effect for CNCOPh.



5: IR, $(\alpha)_D^{25} = +133°$

6a: $(\alpha)_D^{25} = +132°$
6b: $(\alpha)_D^{25} = +115°$

Scheme 1

Substitution of the arene ring in the complex (arene)$Cr(CO)_2L$ according to: (arene)$Cr(CO)_2L + 3\ CO \rightarrow Cr(CO)_5L$ + arene, proved to be easy with L = CS, more difficult with L = CNCOPh and impossible under the same conditions with L = CO and $CNCH_3$.

Certain tricarbonyl chromium complexes are excellent selective catalysts for hydrogenation reactions [7]. The use of similar complexes having the requisite electronic properties and containing chiral chromium centres or (and) chiral carbon ligands offers the possibility of catalytic asymmetric syntheses under mild conditions. Therefore it was of interest to test the catalytic behavior of the alternative to CS new key-ligand CNCOPh. In parallel experiments using (o-OCH_3—C_6H_4—CO_2CH_3)$Cr(CO)_3$ 7 and (o-OCH_3—C_6H_4—CO_2CH_3)$Cr(CO)_2$CNCOPh 8 as catalysts (0.01) the hydrogenation of (methyl-2,4-hexadienoate to methyl-3 hexanoate was studied (temp.: 120°C, pH_2 = 30 atm., acetone, 5 h). While the $Cr(CO)_3$ complex 7 produced a 100% hydrogenation the modified $Cr(CO)_2$CNCOPh unit 8 appeared to be almost as efficient (92%) with no change in selectivity. Work is currently in progress to explore the possibility of preparing new and efficient catalysts for asymmetric synthesis by using the exceptional versatility (by comparison with CO), from both electronic and structural viewpoints, of isocyanide ligands. However, it is clear from the foregoing that a wider scope of applications may be envisaged.

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Our MINDO/3 calculations [13] have shown a greater stabilization of the LUMO π^* in this particular situation. However the effect is similar in the two types of isocyanides.

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A complete optimisation of the free-ligand geometries using the MINDO/3 method has been carried out. In both alkyl and acyl isocyanide, the linear conformation is the most stable. However, as for ab initio calculations, very weak differences were observed between the two conformations (linear and slightly bent).

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