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Preliminary communication

Phosphinic complexes of rhenium and tungsten in reactions with stereoindicators

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Abstract

Stereoindicators (*cis*-4,4′-dimethoxystilbene (DMS) or *cis*-α,β-dinitrostilbene (DNS)) were used to investigate the donor/acceptor properties of the complexes *trans*-[$ReCl(N_2)(dppe)_2$] or *trans*-[$W(CO)_4(dppe)$]. The former induced *cis/trans* conversion of DMS, and the latter *cis/trans* conversion of DNS, both resulting from charge transfer (in the first case from DMS to the rhenium complex and, in the second case, from the tungsten complex to DNS). The rhenium complex acts as an acceptor, and the tungsten complex as a donor in the framework of the stereoindicator approach.

Accumulated material on donor/acceptor properties of organic compounds permits us to compare them on the basis of their structural formulae, with considerable accuracy. However, such an approach has not been established for organometallic compounds. The donor/acceptor properties of only a few metallocomplexes have been elucidated by means of the stereoindicator method applied [1] to a series of isoelectronic acetylacetonate complexes of rhodium with other variable ligands.

In this paper, such a method of comparison is extended to the following complexes of different metals with donor and acceptor ligands: the rhenium dinitrogen complex *trans*-[$ReCl(N_2)(dppe)_2$] (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$) and the tungsten compound *trans*-[$W(CO)_4(dppe)$] (**2**).

The donor or acceptor inclination of the complexes was estimated by the occurrence of the following olefin isomerization reaction:

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Table 1

Interaction of *cis*-4,4′-dimethoxystilbene (*cis*-DMS) or *cis*-α,β-dinitrostilbene (*cis*-DNS) with complexes of Re and W

Stilbene	Solvent	Contact period (h, 20°C)	Degree of *cis*/*trans* conversion (% ±5%)
trans-[ReCl(N_2)($Ph_2PCH_2CH_2PPh_2$)$_2$]			
cis-DMS	C_6D_6	3	26
cis-DMS	C_6D_6	72	27
cis-DNS	C_6D_6	3	0
cis-DNS	C_6D_6	72	0
cis-DMS	$CDCl_3$	3	27
cis-DMS	$CDCl_3$	72	26
cis-DNS	$CDCl_3$	72	0
trans-[W(CO)$_4$($Ph_2PCH_2CH_2PPh_2$)]			
cis-DMS	C_6D_6	72	0
cis-DMS	$CDCl_3$	72	0
cis-DNS	C_6D_6	3	30
cis-DNS	C_6D_6	72	30
cis-DNS	$CDCl_3$	3	29
cis-DNS	$CDCl_3$	72	30

The results, obtained by the stereoindicator method, by using *cis*-4,4′-dimethoxystilbene (DMS) or *cis*-α,β-dinitrostilbene (DNS) as stereoindicators, are shown in Table 1.

The rhenium complex induces the *cis*/*trans* isomerization of DMS but not that of DNS which, however, is promoted by the tungsten complex. Moreover, the nature of the solvents used (chloroform or benzene) and the contact durations have no effect on the degree of conversion, and the metal complexes do not change during the reaction (as monitored by ^{1}H NMR and IR methods for the initial complexes, the complexes contacting with a stereoindicator, and the complexes at the end of the exposure).

Decreasing the metallocomplex amounts to *ca.* 0.1–0.05 times the equimolecular amount prevents isomerization during exposure (see Table 1).

ESR signals are not observed in the probes of reaction solutions. The formation of charge-transfer complexes was established when the colour deepened, as a result of the components mixing; for the tungsten complex **2**, the charge-transfer band at 370 nm (with DNS) was revealed.

Blank experiments have shown the absence of *cis*/*trans* isomerization of the stereoindicators in the above-mentioned solvents, upon treatment of the olefin solution with bis(diphenylophosphino)ethane.

Thus, the following conclusions may be inferred:

(i) the rhenium complex **1** behaves as an acceptor whilst the tungsten complex **2** is essentially a donor;

(ii) the action of the stereoindicator is realized through its donor-acceptor interaction with the metallocomplex as a whole, and a catalytic effect does not take place;

(iii) essential changes of the metallocomplex coordination sphere, in the presence of a stereoindicator, have not been detected.

This study indicates the danger associated with the generalization of the electron donor/acceptor ability of a complex based on chemical behaviour towards a particular type of reagent. In fact, although a variety of isocyanide, nitrile or alkyne-derived complexes with the electron-rich {ReCl(dppe)$_2$}site of the type *trans*-[ReCl(L)(dppe)$_2$] (L = CNR, NCR, C=CHR), which are isoelectronic with the rhenium-dinitrogen complex of this study, are susceptible to electrophilic attack by H^+ [3], the above-mentioned results demonstrate that, in contrast, complexes of this type can also behave as electron-acceptors towards a suitable electron-donor substrate, such as an adequately activated olefin. The implication of these observations, in terms of chemical reactivity towards nucleophiles, should be explored.

Experimental

The tungsten [3] and the rhenium [4] complexes, α,β-dinitrostilbene (*cis* or *trans*) [5] and 4,4′-dimethoxystilbene (*cis* or *trans*) [6] were synthesized according to literature procedures.

The ^1H NMR spectra were recorded on a Bruker WP-200 SY spectrometer and the IR spectra on a Bruker IFS-113 instrument.

Stilbene (*cis* form) and metallocomplex were dissolved in benzene-d_6 or $CDCl_3$. Orange solution mixtures were obtained from practically colourless separated solutions. The solution mixtures were placed in ^1H NMR tubes sealed under argon. The ^1H NMR spectra were recorded after 3 and 72 h. In respect of the metallocomplexes, the ^1H NMR were unchanged throughout the contact time, for the stereoindicators the ^1H NMR resonances changed as expected where *cis*/*trans* isomerization occurred. The degree of conversion was estimated by comparing the appropriate resonance intensities of the *cis* and *trans* isomers. Comparison of the IR spectrum of the rhenium complex (in KBr pellets) with that in the presence of a stereoindicator (solution in benzene) revealed that no frequency changes occurred in the range 720–1980 cm^{-1}. Integrity control of the tungsten complex was fulfilled in the same manner (IR frequencies in the range 1886–2022 cm^{-1}).

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