# DONOR PROPERTIES OF cis-DIPYRIDINETUNGSTEN TETRACARBONYL

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it is converted to the trans form.

 $cis-\alpha$ -Nitrostilbene can be used as an indicator to distinguish donor molecules by their ability to transfer an electron completely or to transfer a charge partially [1]. In electron transfer (where the donor is cyclooctatetraene anion),  $cis-\alpha$ -nitrostilbene dimerizes; with charge transfer (where the donor is an aromatic amine)

It was of interest to check the behavior of  $cis-\alpha$ -nitrostilbene in the presence of metal complexes with donor ligands. The first complex to be investigated was the W(0) complex cis-dipyridinetungsten tetracarbonyl. It was found that in the presence of an equimolar amount of this complex cis- $\alpha$ -nitrostilbene does not form the hydrodimer (even in trace amounts), but is converted to the trans isomer. The half-conversion period is 3 h at 25°C; the reaction does not require illumination and takes place even at 4°C:



UDC 541.128:541.49:546.785:

547.82:547.636.3

Special tests showed that treatment of  $ci - \alpha$ -nitrostilbene in THF solution with pyridine or CO does not form the trans isomer.\* Products of nitro group reduction were not found. Complex I was also converted quantitatively without change of geometry. Nor was any change in the complex detected during the reaction; the IR absorption bands of CO were monitored every 15-20 min. During the reaction a charge transfer complex (CTC) is formed between tungsten and nitrostilbene that was detected spectrophotometrically by the charge transfer bands at 370 and 500 nm. The detection of CTC by the electronic spectrum but not by IR means that the steady state CTC concentration is small. The cis-trans isomerization of nitrostilbene under the action of the tungsten compound proceeds under very mild conditions. The reversible formation of a nitrostilbene-carbonyl complex of tungsten is unlikely, since olefin-carbonyl complexes of molybdenum and tungsten yield a mixture of olefin and metal carbonyl upon UV-irradiation or heating [2, 3]. No cases are known where nitroolefins form complexes with transition metals in zero oxidation state. The reaction of phenyl  $\omega$ -nitrovinyl ketone with Fe<sub>2</sub>(CO)<sub>9</sub> [4] proceeds like an oxidation-reduction reaction, and nitrovinyl ketone gives a polymer. Therefore  $\pi$ -bonding of the nitroolefin with tungsten (as in metal  $\pi$ -complexes) seems unlikely in the reaction we are studying. On the other hand, it can be assumed that CTC formation precedes the reaction of  $\alpha$ -nitrostilbene with the tungsten complex in which the nitroolefin transfers a proton to the W(0) complex;

$$Py_2W(CO)_4 + \text{cis} -PhCH = C(Ph)NO_2 \rightarrow [Py_2W(CO)_4H]^+ + \text{trans} -Ph\overline{C} =$$

$$= C(Ph)NO_2 \rightarrow Py_2W(CO)_4 + \text{trans} -PhCH = C(Ph)NO_2$$
(2)

But treatment of the reaction mixture with  $D_2O$  does not yield any products containing C-D bonds, as shown by mass spectrometry and analysis of water of combustion; this is evidence that mechanism (2) does not occur. Moreover, isomerization was detected also when the stereoindicator was  $cis-\alpha$ ,  $\beta$ -dinitrostilbene, viz. a compound containing no vinyl protons at all. In such a compound it is impossible to assume removal and reversible addition of a NO<sub>2</sub> group.

\* Cis-trans isomerization was not found when catalytic amounts of (I) were used, when the  $Py_2W(CO)_4$ : PhCH =  $C(NO_2)$ Ph ratio was 1:10 instead of equimolar.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1388-1390, June, 1982. Original article submitted July 27, 1981. It can be assumed that the reason for the observed cis-transisomerization under the action of cis-dipyridinetungsten tetracarbonyl is the formation of a charge transfer complex.

#### EXPERIMENTAL

cis- $\alpha$ -Nitrostilbene was synthesized by the procedure of [5]. It was purified by recrystallization from hexane and identified by a mixed melting point with a known sample, mp 71-72°C (cf. [5]). UV spectrum (THF),  $\lambda$  318 nm ( $\epsilon$  1 · 10<sup>4</sup>); PMR (CCl<sub>4</sub>, TMS external standard,  $\delta$ , ppm) 7.4 m (10 H, C<sub>6</sub>H<sub>5</sub>), 8.15 s (1 H, CH).

For the synthesis of  $Py_2W(CO)_4$ , 0.101 g of  $Py_3W(CO)_3$ , obtained by the procedure of [6], was stirred with 20 ml of THF or CHCl<sub>3</sub> at ~20°C. Within 20 min the precipitate dissolved to form a yellow solution, the IR spectrum of which contains the following bands: 2012, 1879 (broad), 1848 cm<sup>-1</sup> (THF) or 2015, 1893, 1876, 1836 cm<sup>-1</sup> (CHCl<sub>3</sub>). These bands correspond to the structure of cis- $Py_2W(CO)_4$  with  $C_{2V}$  symmetry [7]. Since no extraneous bands whatever were present in the complex spectrum, the solution was used in the subsequent tests without separating the cis-dipyridine complex or subjecting it to further purification. The synthesis was analogous to the fac- $L_3M(CO)_3 \rightarrow cis-L_2M(CO)_4$  conversion, which is well known for complexes of the chromium sub-group [8].

A solution of 2 mmole of cis- $\alpha$ -nitrostilbene in 10 ml of THF was stirred with a solution of 2 mmole of cis-dipyridinetungsten tetracarbonyl in 20 ml of THF at ~20°C in a stream of purified Ar. A reddish color appeared. After 25 h the reaction mixture was evaporated in vacuum and the residue was separated on Al<sub>2</sub>O<sub>3</sub> (3:4 hexane-ether eluent). The tungsten complex remained at the start, 100% yield; when eluted with benzene, it was completely identical with the starting material. cis- $\alpha$ -Nitrostilbene was eluted with ether (band with Rf 0.83, ether evaporated, yield 36.6%). trans- $\alpha$ -Nitrostilbene was also eluted with ether (band with Rf 0.63, yield 63.3%). The isolated isomers were compared with known samples by TLC, melting point, and IR spectra. The reference samples of the tungsten complex were dissolved in THF in an Ar atmosphere. The IR spectrum was taken every 4-6 h for 1 day. It was established that the dipyridine complex did not undergo cis-trans isomerization or other changes. The IR and UV spectra of the reaction mixtures and the starting materials were measured in THF solution in UR-20 and Hitachi EPS-3T apparatus, respectively. To find the hidden charge transfer bands we compared the experimental and calculated optical densities of a mixture of nitrostilbene and the tungsten complex (D<sub>mix</sub>). The calculated values were found by

## $D_{\text{mix}} = (D_{\text{ns}} + D_{\text{c}})/2$

where  $D_{ns}$  is the optical density of a  $10^{-2}$  mole/liter solution of cis- $\alpha$ -nitrostilbene in THF;  $D_c$  is the optical density of a  $10^{-2}$  mole/liter solution of  $Py_2W(CO)_4$  in THF; and  $D_{mix}$  is the optical density of a THF solution containing an equimolar mixture of the components at a total concentration of  $10^{-2}$  mole/liter. Experimental values of  $D_{mix}$  were determined directly from the absorption spectrum of the mixture. The charge transfer band was detected from a plot of  $D_{mix}(exp)/D_{mix}(calc)$  vs.  $\lambda(nm)$ .

### CONCLUSION

In the reaction of  $cis-\alpha$ -nitrostilbene with cis-dipyridinetungsten tetracarbonyl, the nitrostilbene is converted to the trans form, while the tungsten complex is not changed.

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