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Preliminary communication

PHOTOCHEMICAL ISOMERIZATION OF CYCLOPENTADIENYLMETAL COMPLEXES

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Summary

The linkage isomers CpM(CO)$_n$SCN and CpM(CO)$_n$NCS (Cp = η-C_5H_5; M = Fe, n = 2; M = Mo, n = 3) are interconverted by 366 nm irradiation in tetrahydrofuran solution at 30°C. Molybdenum and tungsten halide complexes CpM(CO)$_2$(PPh$_3$)X undergo *cis—trans* isomerization and disproportionation to CpM(CO)$_3$X and CpM(CO)(PPh$_3$)$_2$X under similar conditions (benzene solution).

Photochemical linkage and geometrical isomerizations of classical coordination complexes have been the subject of considerable recent interest [1, 2]. These phenomena have received surprisingly little attention in organometallic systems to date [3]. The linkage isomerizations shown in eqns. 1 and 2 have been achieved by photolysis* of the respective pure isomers [4] in tetrahydrofuran solution at 30 ± 2°C. The iron complexes are reported to be stable thermally under these conditions [4] and appropriate blank reactions carried out in conjunction with the photolyses confirm this. The interconversions are conveniently followed by infrared spectroscopy in the C—N and C—O stretching regions as shown in Fig. 1.

$$\mathrm{CpFe(CO)_2NCS} \underset{h\nu}{\overset{h\nu}{\rightleftharpoons}} \mathrm{CpFe(CO)_2SCN} \qquad (1)$$

$$\mathrm{CpMo(CO)_3NCS} \xrightleftharpoons[h\nu \text{ or } \Delta]{h\nu} \mathrm{CpMo(CO)_3SCN} \qquad (2)$$

The photostationary state for the iron isomers is approximately a 1/1 mixture. Once formed, the isomeric mixtures persist in solution, consistent with their thermal stability.

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*Rayonet Type RS-5 Reactor fitted with Rul-3500 Lamps and a standard Merry-Go-Round apparatus. All reactions were conducted in sealed, degassed 12 mm Pyrex tubes. Solutions were 10^{-3}-10^{-4} *M*, irradiated 1-2 hours.

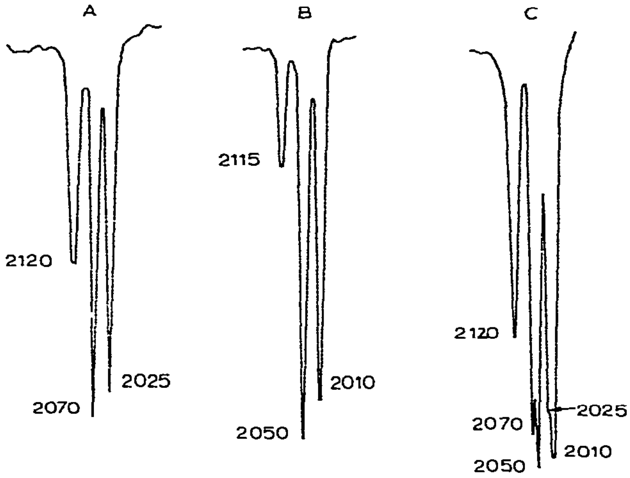

Fig. 1. Infrared spectra of: A, $CpFe(CO)_2NCS$, B, $CpFe(CO)_2SCN$; C, Product mixture. Chloroform solution 0.1 mm KBr cells.

Similar results were obtained for the molybdenum system (eqn. 2) although in this case thermal conversion of the S-bonded to N-bonded isomer is a minor complication. Control experiments in the absence of light indicate that approximately 10% of the isomerization is thermal in origin. The reverse process (N-bonded → S-bonded) does not occur thermally, as previously noted [4]. To our knowledge these are the first examples of photochemically induced linkage isomerizations of the thiocyanate ligand.

Photolyses of the complexes $CpM(CO)_2(PPh_3)X$ (M = Mo or W, X = halide) at 366 nm in benzene solution (10^{-3} *M*) lead to *cis—trans* isomerization* and "disproportionation" to $CpM(CO)_3X$ and $CpM(CO)(PPh_3)_2X$ (Table 1).

TABLE 1

PHOTOLYSIS OF $CpM(CO)_2(PPh_3)X$ COMPLEXES

Complex [a]	% *trans*	% *cis*	Irradiation time (h)	Added ligand	Product distribution (%) [b]		
					$CpM(CO)_3X$	$CpM(CO)_2LX$ *cis/trans*	$CpM(CO)(L)_2X$
$CpMo(CO)_2(PPh_3)Br$	65	35	22	—	12	74/9	4
$CpMo(CO)_2(PPh_3)Br$	0	100	22	—	12	68/8	12
$CpMo(CO)_2(PPh_3)Br$	0	100	22	PPh_3 [c]	0	10/0	90
$CpMo(CO)_2(PPh_3)I$	100	0	22	—	13	49/27	11
$CpMo(CO)_2(PPh_3)I$	0	100	22	—	9	54/22	15
$CpMo(CO)_2(PPh_3)I$	50	50	3	—	13	52/24	11
$CpMo(CO)_2(PPh_3)I$	50	50	3	CO [d]	23	47/30	0
$CpMo(CO)_2(PPh_3)I$	50	50	3	PPh_3 [e]	0	28/23	49
$CpMo(CO)_2(PPh_3)I$	50	50	22	PPh_3 [e]	0	13/10	77
$CpW(CO)_2(PPh_3)I$	100	0	22	—	6	76/18	0 [f]
$CpW(CO)_2(PPh_3)I$	0	100	22	—	6	75/19	0 [f]
$CpW(CO)_2(PPh_3)I$	38	62	22	PPh_3 [c]	0	10/0	90

[a] 10^{-3} *M*, benzene solution. [b] Determined by integration of C_5H_5 region, Varian T-60 NMR spectrometer. Presence of $CpM(CO)_3X$ and $CpM(CO)(PPh_3)_2X$ confirmed by IR. [c] PPh_3 : M ratio 3 : 1. [d] 1 atm, CO : Mo ratio ~ 6 : 1. [e] PPh_3 : Mo ratio 1.5 : 1. [f] Not detectable by NMR; IR shows trace amounts.

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*Pure isomers were prepared as previously described [5].

Appropriate control reactions have shown that these processes do not occur at 30°C in the absence of light. Evidence has been presented that thermal *cis*$\rightleftharpoons$*trans* interconversions of these and related complexes are intramolecular in nature [6, 7]. The accompanying formation of $CpMo(CO)_3X$ and $CpM(CO)(PPh_3)_2X$ noted here suggests that ligand dissociation (eqns. 3 and 4) may be an important pathway in the photochemical isomerization process. Recombination of the

$$CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)(PPh_3)X + CO \qquad (3)$$

$$CpM(CO)_2(PPh_3)X \xrightarrow{h\nu} CpM(CO)_2X + PPh_3 \qquad (4)$$

sixteen-electron complexes $CpM(CO)_2X$ and $CpM(CO)(PPh_3)X$ with CO or PPh_3 could account for the spectrum of products observed and the *cis*$\rightleftharpoons$*trans* interconversions. Carbon monoxide dissociation has been shown to be a dominant photoprocess for $CpMo(CO)_3Cl$ [8] and $CpMo(CO)_3Br$ [9] and competitive loss of CO vs. other two-electron ligands dominate the photochemistry of octahedral Group VI carbonyls [3]. Competition experiments with added CO and PPh_3 (Table 1) indicate that both reagents effectively scavenge the proposed coordinatively unsaturated intermediates. The data currently at hand do not allow definitive conclusions as to whether CO or PPh_3 dissociation (or both) are responsible for the observed isomerizations. Further studies on the mechanisms of these processes, including photolyses at longer wavelengths, are in progress.

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