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Preliminary communication

ISOMERICALLY PURE CYCLOPENTADIENYL-MOLYBDENUM AND -TUNGSTEN CARBONYL HALIDE COMPLEXES

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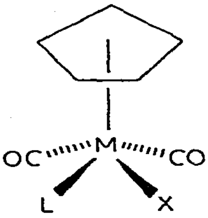
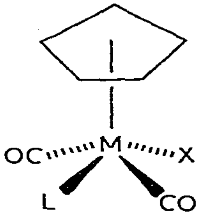
Summary

Pure *cis*- and *trans*-(η^5-C_5H_5)M$(CO)_2$[P$(C_6H_5)_3$]X (M = Mo, X = I or Br; M = W, X = I) have been separated by chromatographic methods. Stereochemical assignments are made on the basis of infrared and ^{1}H and ^{13}C NMR spectroscopy. Mechanistic implications of the *cis/trans* isomer ratios as a function of the method of preparation are discussed.

Complexes of the general formula CpM$(CO)_2$(L)X (Cp = η^5-C_5H_5; M = Mo or W; L = a phosphine or phosphite; X = halide, alkyl or hydride) have been shown to exist as *cis* (I) and *trans* (II) isomers. The relative proportions of these isomers depend markedly on the nature of L and X [1-3] but the factors determining the *cis/trans* ratio have not been resolved. The separation of such isomeric mixtures into their components is essential to the study of these phenomena, and although the possibility of such separations has been alluded to in a preliminary report [4], details were not given. King, Reimann and Darensbourg [5] have recently described the successful chromatographic separation of isomers of the structurally similar CpRe$(CO)_2Br_2$. We report herein the separation and isolation of the pure *cis*- and *trans*-isomers of



(I)



(II)

$CpM(CO)_2[P(C_6H_5)_3]X$ (M = Mo, X = I or Br; M = W, X = I)*.

The complexes were prepared by reaction of the appropriate cyclopentadienylmetal tricarbonyl halide with triphenylphosphine in refluxing benzene or toluene [7-9] (eqn. 1), and by reaction of acetyl complexes with bromine or iodine in chloroform at 0°C [10,11] (eqn. 2). Chromatography of the reaction products (Brockman Activity Grade I alumina, 50.0 × 3.0 cm column, 1/1 benzene/hexane eluent) afforded orange (*cis* isomers) and red-purple bands (*trans* isomers) in all cases. The *cis/trans* isomer ratio was a function of the halogen and the method of preparation (Table 1).

$$C_5H_5M(CO)_3X + P(C_6H_5)_3 \rightarrow C_5H_5M(CO)_2P(C_6H_5)_3X + CO \qquad (1)$$

$$trans\text{-}C_5H_5M(CO)_2[P(C_6H_5)_3]COCH_3 + X_2 \rightarrow C_5H_5M(CO)_2[P(C_6H_5)_3]X \qquad (2)$$

The *cis* and *trans* isomers afford singlet and doublet ($J(PH)$ = 1.5-2.0 Hz) C_5H_5 resonances respectively in their proton NMR spectra (Table 2). This criterion has been shown to be diagnostic for the assigned stereochemistries [1-3]. Further support of the assignments made comes from the relative intensities of the infrared carbonyl stretching frequencies [8,12]. For the *cis* isomers the higher frequency (*sym*) CO stretch is more intense than the lower frequency (*antisym*) stretch, while the opposite is true for the *trans* isomers (Table 2). Any residual doubt concerning the identity of the isolated complexes is removed by consideration of the ^{13}C NMR spectra. A single CO

TABLE 1

ISOMER RATIOS AS A FUNCTION OF METHOD OF PREPARATION [a]

Complex	Thermal substitution [b] (*cis/trans*)	Halogen cleavage (*cis/trans*)
$CpMo(CO)_2[P(C_6H_5)_3]Br$	95/5	36/64
$CpMc(CO)_2[P(C_6H_5)_3]I$	65/35	40/60
$CpW(CO)_2[P(C_6H_5)_3]I$	65/35	35/65

[a] Determined by integration of NMR spectra in the C_5H_5 region. Varian T-60 Spectrometer, $CDCl_3$ solution. (See text for discussion). [b] Determined immediately after consumption of $CpM(CO)_3X$.

TABLE 2

PHYSICAL AND SPECTROSCOPIC DATA

Complex	Color	M.p. (°C)	$\delta(C_5H_5)$ [a]	$\nu(CO)$ (cm^{-1}) [b]
cis-$CpMo(CO)_2[P(C_6H_5)_3]Br$	orange	183d	5.37s	1980vs 1890s
trans-$CpMo(CO)_2[P(C_6H_5)_3]Br$	red-purple	185d	5.08 (d, $J(PH)$ 1.5)	1980s 1890vs
cis-$CpMo(CO)_2[P(C_6H_5)_3]I$	orange	172d	5.34s	1972vs 1890s
trans-$CpMO(CO)_2[P(C_6H_5)_3]I$	red-purple	176d	5.11 (d, $J(PH)$ 2.0)	1972s 1890vs
cis-$CpW(CO)_2[P(C_6H_5)_3]I$	orange	186d	5.47s	1960vs 1876s
trans-$CpW(CO)_2[P(C_6H_5)_3]I$	red	193d	5.15 (d, $J(PH)$ 2.0)	1960s 1876vs

[a] Varian Associates T-60 spectrometer, $CDCl_3$ Solvent. Chemical shifts in ppm downfield from internal TMS; s=singlet, d=doublet, $J(PH)$ in Hz. [b] Perkin-Elmer 521 Spectrophotometer, $CHCl_3$ solution, matched 0.1 mm KBr cells.

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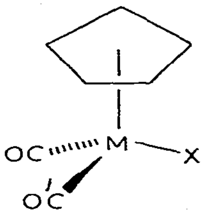
*Related cationic carbene complexes have been prepared as pure *cis* and *trans* forms, but this process did not involve isomer separation [6].

resonance (δ 232.4 ppm, doublet, J(PC) 27.4 Hz) is observed for *trans*-CpMo(CO)$_2$[P(C$_6$H$_5$)$_3$]I. For the *cis* isomer two equally intense CO resonances (δ 250.3 ppm, doublet, J(PC) 28.6 Hz, δ 236.8 ppm, doublet, J(PC) 5.0 Hz) are observed. Similar data are obtained for the other complexes. The expected Cp and phenyl carbon resonances are observed in all cases. Details of these and related results will be the subject of a future publication [13].

The complexes are stable with respect to isomerization in both the solid state and in solution at or near room temperature. However, when solutions of the pure *cis*- and *trans*-CpMo(CO)$_2$[P(C$_6$H$_5$)$_3$]I in benzene are heated to 80 °C, rapid isomerization occurs. Based on integrations of the cyclopentadienyl resonances in the proton NMR spectra of the complexes, both *cis* and *trans* isomers show 40% isomerization after one hour and reach 50/50 *cis/trans* equilibrium mixtures after 24 h. Similar observations were made for the tungsten iodide complex, although isomerization proceeds more slowly in this case. The equilibrium position in the case of CpMo(CO)$_2$[P(C$_6$H$_5$)$_3$]Br (refluxing benzene) is 95% *cis*, 5% *trans*.

An intersting aspect of the stereochemical results is the dependence of the *cis/trans* isomer ratio on the method of preparation. (Table 1). That the thermal substitution reactions afford predominantly the *cis* modification may be explained as follows. Statistically, the presumed coordinately unsaturated intermediate III [14] would afford 67% *cis* and 33% *trans*, since attack of phosphine between CO and X is twice as likely as attack between the two carbon monoxide ligands. This postulate (while consistent with the data at hand) is regarded as tenuous and more detailed studies are in progress. The halogen cleavage reactions (equation 2) afford a high percentage of the respective *trans* isomers, suggesting retention of stereochemistry at the metal atom. Mechanistic speculation regarding these processes would be premature at this time, although the results are consistent with the electrophilic attack scheme recently suggested for related iron complexes [15]. Detailed examinations of these systems and extensions of the cleavage reactions to previously inaccessible *trans* complexes are in progress.



(III)

Acknowledgements

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