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Preliminary communication

Organometallic conformational equilibria
XII. Racemization in derivatives of π-cyclopentadienylmolybdenum and π-indenylmolybdenum tricarbonyl dimers*

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The coordination geometry about the molybdenum atom in π-indenyl-Mo(CO)$_2$LR compounds can be conveniently described as a square pyramid with the indenyl moiety at the apex and the remaining ligands at the corners of a square base. The possible geometric arrangements of the L, R, and two carbonyl ligands about the corners of the square allows for one *trans* and two enantiomeric *cis* isomers. As with the cyclopentadienyl analogs[1-4] these complexes undergo intramolecular rearrangements which interchange the ligands and thus provide pathways for interconversion of isomers. On the NMR time scale, two distinct processes, *cis–trans* isomerization and *cis–cis* racemization, may be observed.

Previous work[1] has indicated that the most likely intermediate for rearrangement would resemble a trigonal bipyramid with one axial position occupied by the π-indenyl or π-cyclopentadienyl moiety and the other axial position occupied by one of the ligands. The goal of these studies is the determination of the relative barrier heights encountered by different ligands assuming the axial position. If either an R or L group occupies such a position a plane of symmetry exists in the intermediate. If, however, a carbonyl ligand is axial there is no plane of symmetry and thus the intermediate is chiral. The type of intermediate involved in rearrangement may be determined, therefore, from a study of the racemization pathway of the *cis* enantiomer. The intermediate with an axial carbonyl remains chiral and racemization via this intermediate must proceed by conversion to the achiral *trans* isomer. On the other hand, an intermediate with two equatorial carbonyls is achiral and thus provides a path for direct interconversion of one *cis* enantiomer. Although *cis*→*cis* enantiomer interconversion in these compounds usually occurs through a pathway with a substantially lower barrier than that for the *cis*→*trans*→*cis* pathway, studies to be discussed here demonstrate that this is not always the case. For π-indenyl-Mo(CO)$_2$P(OMe)$_3$I, the barriers for the two paths are of approximately the same height.

The PMR of the *cis* isomer of π-cyclopentadienyl-Mo(CO)$_2$ [P(CH$_3$)$_2$C$_6$H$_5$]I showed two methyl resonances, presumably diastereotopic due to a chiral center at the molybdenum atom, separated by 0.2 ppm. These resonances broaden and average before

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*For part XI see ref. 1.

any significant exchange between *cis* and *trans* isomers is indicated by broadening of the resonances assigned to the *trans* isomer. This complex first led to the proposal that *cis*→*cis* enantiomer interconversion occurred without intermediate formation of the *trans* isomer; hence, that the intermediate responsible for the interconversion did not contain an axial carbonyl. An investigation of the indenyl complexes was initiated to demonstrate that this averaging is truly due to *cis*–*cis* enantiomer interconversion rather than hindered rotation about the Mo–P bond or inversion at the phosphorus atom.

Although one anticipates that the indenyl moiety would have a plane of symmetry, the chiral center at the molybdenum atom in the *cis* isomer makes the "equivalent" protons diastereotopic and all seven protons nonequivalent. This is most evident in the cyclopentadienyl portion of the indenyl ligand, *e.g.*, there is a 0.6 ppm chemical shift difference between the 1 and 3 protons in π-$C_9H_7Mo(CO)_2P(CH_3)_2C_6H_5I$* as seen in Table 1.

Upon raising the temperature the 1 and 3 protons average at the same rate as do the nonequivalent methyl groups, at δ 1.70 ($J = 8.3$ Hz) and δ 1.6 ($J = 9.1$ Hz) of the dimethylphenylphosphine ligand. This provides strong evidence that the nonequivalence of the methyl groups $P(CH_3)_2C_6H_5$ arises from the chirality of the molecule rather than hindered rotation about the Mo–P bond in *cis* isomers of either π-indenyl or π-cyclopentadienyl complexes.

Further evidence that the process responsible for averaging of the methyl resonances of $P(OCH_3)_2C_6H_5$ and $P(CH_3)_2C_6H_5$ ligands in *cis*-π-$C_9H_7Mo(CO)_2LR$ (and π-$C_5H_5Mo(CO)_2LR$) does not involve an inversion at the phosphorus atom is found in the PMR spectrum of π-$C_5H_5FeCOP(CH_3)_2C_6H_5I$. Only inversion of configuration at the iron atom or inversion of the phosphine ligand itself could average the methyl environments. Since no averaging of the methyl resonances in the PMR spectrum is observed at temperatures up to 190°, where decomposition is too rapid for observation of a spectrum, no inversion has occurred. If no inversion of the phosphorus ligand occurs in the iron compound, it is unlikely that it is occurring in the molybdenum compounds at a much lower temperature.

Previous work[1] demonstrated that the barriers to rearrangement processes in these stereochemically nonrigid molecules may be reliably calculated from the Eyring equation, $k = k_B T/h \exp(-\Delta F^*/RT)$. ΔF^* for π-$C_5H_5Mo(CO)_2LR$ has been calculated by averaging a minimum of three rates taken at three temperatures (see Tables 2 and 3). Since ΔS^* is very small in all cases, ΔF^* varies by less than 0.5 kcal/mole over a temperature range of 100 degrees.

Comparison of thermodynamic data indicates that the *cis* isomer is generally more favored in the indenyl compound than in the corresponding cyclopentadienyl analog. There are not sufficient data at this time to warrant generalizations about comparisons of kinetics because *cis*–*cis* barriers could not be measured in most of the cyclopentadienyl complexes. Of particular interest, however, is the observation that the free energy of activation of the *cis*→*cis* interconversion depends markedly on the halide, whereas the *cis*→*trans* barriers are relatively independent of the halide. This is illustrated for the Cl, Br, and I derivatives of $C_5H_5Mo(CO)_2P(CH_3)_2C_6H_5$ in Table 2. The increasing values of ΔF^* with $Cl < Br < I$ reflects the importance of steric factors in determining relative barrier heights.

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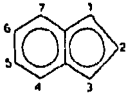
*It is assumed that rotation of the indenyl fragment relative to the Mo-containing moiety is rapid on the NMR time scale.

(*continued on* p.C52)

TABLE 1

PROPERTIES OF SOME INDENYLMOLYBDENUM COMPLEXES

$C_9H_7Mo(CO)_2LI$ [a] L						$\Delta F^*c\rightarrow c$ (kcal/mole (°C))	$\Delta F^*c\rightarrow t$ [b] (kcal/mole (°C))	$K_{eq} \equiv \frac{[cis]}{[trans]}$ [c]
	δ_1	δ_3	δ_2	$\delta_{4,5,6,7}$	J_{12}			
$P(CH_3)_2C_6H_5$	5.77	5.14	4.84	~7.4	3.0	21.3 (110)	23.4 (110)	7.5
$SbPh_3$ [f]	5.93	5.46	4.88	~7.4	3.0	21.0 (110)	–	
PPh_3 [f]	5.84	5.15	4.86	~7.4	3.0	23.2 (130)	–	
$P(OCH_3)_3$ [f]	~5.6 [d]	~5.6 [d]	4.91	~7.4	2.9	20.6 [d,e] (100)	20.4 (100)	0.79

[a] *Cis* isomer at 31° in *o*-dichlorobenzene. [b] Calculated from Eyring equation from rates obtained within ± 10° of reported temperature. [c] In *o*-dichlorobenzene at +31°. [d] Resonances 1 and 3 appear under the corresponding resonances of *trans* isomer so that $\Delta F^*c\rightarrow c$ may not be measured in *o*-dichlorobenzene. [e] In $CHBr_3$ resonances of *cis* and *trans* isomers are not superposed. [f] These complexes were prepared concurrently by other workers[5]; however, no *trans* isomers nor rearrangements were observed.

TABLE 2

PROPERTIES OF SOME π-CYCLOPENTADIENYLMOLYBDENUM COMPLEXES

π-$C_5H_5Mo(CO)_2LR$					
R	L	ν(CO)(cm^{-1}) (in C_6H_{12})	$K_{eq} \equiv \frac{[cis]}{[trans]}$ (in $CDCl_3$ at 31°)	$\Delta F^*c{\to}c$ [a] (kcal/mole (°C))	$\Delta F^*c{\to}t$ (kcal/mole (°C))
H	$P(CH_3)_2C_6H_5$	1951, 1941, 1865	0.92	–	13.6 (25)
Cl	$P(CH_3)_2C_6H_5$	1983, 1886	31	18.9 (65)	–
Br	$P(CH_3)_2C_6H_5$	1981, 1888	8.2	20.1 (90)	25.8 (160)
I	$P(CH_3)_2C_6H_5$	1976, 1889	4.7	21.6 (110)	25.4 (160)
CH_3	$P(CH_3)_2C_6H_5$	1949, 1941, 1860	0.17	19.9 (90)	20.7 (100)
H	$P(OCH_3)_2C_6H_5$	1968, 1895	7.5	12.1 (–50)	13.9 (–20)
Cl	$P(OCH_3)_2C_6H_5$	1989, 1907	14	18.2 (50)	23.4 (120)
Br	$P(OCH_3)_2C_6H_5$	1988, 1906	6.2	19.3 (70)	23.7 (120)
I	$P(OCH_3)_2C_6H_5$	1984, 1913, 1907	1.1	20.7 (90)	23.2 (120)
CH_3	$P(OCH_3)_2C_6H_5$	1958, 1882	0.26	19.5 (80)	19.7 (80)
$C_6H_5CH_2$	$P(OCH_3)_2C_6H_5$	1953, 1877	0.08		

[a] Calculated from $k = k_BT/h \exp(-\Delta F^*/RT)$ using three rates within a ± 10° range of the indicated temperature and averaging the values of ΔF^*. Values of ΔF^* are reproducible to better than 0.2 kcal/mole: this error is greater than that introduced in assuming that $\Delta F^* = \Delta H^* - T\Delta S^* \cong \Delta H^*$. Previous studies[1] indicate that ΔS^* is small causing changes of less than 0.1 kcal/mole over a 20° range.

TABLE 3

PMR DATA FOR SOME π-CYCLOPENTADIENYLMOLYBDENUM COMPLEXES

π-$C_5H_5Mo(CO)_2LR$		*trans*-π-C_5H_5 $\delta(J(PH))$ [a]	*cis*-π-C_5H_5 $\delta(J(PH))$	*trans* L–methyl $\delta(J(PH))$	*cis* L–methyl $\delta(J(PH))$	*trans* R $\delta(J(PH))$	*cis* R $\delta(J(PH))$
R	L						
H	$P(CH_3)_2C_6H_5$	4.98 (1.0)	5.22 (<0.3)	1.82 (8.8)	1.77 (9.0) [b]	−6.06 (23.3)	−6.15 (65.6)
Cl	$P(CH_3)_2C_6H_5$	4.99 (2.4)	5.33 (0.5)	–	1.85 (9.7), 1.81 (9.4)	–	–
Br	$P(CH_3)_2C_6H_5$	4.98 (2.3)	5.31 (0.5)	1.94 (8.9)	1.97 (9.0), 1.94 (8.7)	–	–
I	$P(CH_3)_2C_6H_5$	5.03 (2.3)	5.29 (0.5)	1.93 (9.1)	2.10 (8.9), 2.06 (8.7)	–	–
CH_3	$P(CH_3)_2C_6H_5$	4.71 (1.4)	5.08 (<0.3)	1.82 (8.5)	1.68 (8.2), 1.65 (8.0)	0.30 (2.8)	−0.18 (11.8)
H	$P(OCH_3)_2C_6H_5$	5.04 (0.9)	5.22 (<0.2)	3.59 (12.7)	3.54 (13.6), 3.42 (11.7)	−6.10 (23.4)	−6.49 (63.2)
Cl	$P(OCH_3)_2C_6H_5$	5.09 (2.3)	5.33 (<0.2)	3.73 (12.6)	3.68 (13.5), 3.60 (11.5)	–	–
Br	$P(OCH_3)_2C_6H_5$	5.09 (2.4)	5.32 (<0.2)	3.74 (12.6)	3.66 (13.7), 3.58 (11.8)	–	–
I	$P(OCH_3)_2C_6H_5$	5.08 (2.3)	5.30 (<0.2)	3.76 (12.1)	3.62 (13.0), 3.55 (11.7)	–	–
$C_6H_5CH_2$	$P(OCH_3)_2C_6H_5$	4.69 (1.6)	4.90 (<0.2)	3.53 (11.9)		2.78 (2.9) [c]	
CH_3	$P(OCH_3)_2C_6H_5$	4.84 (1.6)	5.05 (<0.2)	3.62 (12.5)	3.46 (13.0), 3.42 (11.8)	0.32 (3.0)	−0.21 (11.6)

[a] All chemical shifts are given in ppm downfield from TMS; coupling constants are given in hertz. NMR spectra were measured at 31° in deuteriochloroform at 100 MHz except for the species R = H, L = $P(CH_3)_2C_6H_5$ (determined at −50°) and R = H, L = $P(CH_3)_2C_6H_5$ (determined at −65° in Cl_2CHF). [b] Although these methyl groups appear accidentally equivalent in this solvent, separate resonances may be observed in a mixture of toluene/dichlorofluoromethane at −75°. [c] Only methylene resonances are reported for R = substituted methyl.

These results corroborate our previous proposal that steric factors are important in determining both thermodynamic and kinetic parameters and, at least for the cyclopentadienyl complexes, *cis*→*cis* occurs more readily than *cis*→*trans* interconversion. There is a delicate balance of interactions, as indicated by the indenyl complexes, which suggest that by sufficient modification of structure the preferred route of racemization can be altered. Nevertheless, the direct *cis*→*cis* mode of racemization is dominant in the cyclopentadienyl complexes and on the basis of our model[1], this rearrangement should occur by the movement of R or L rather than a carbonyl to the apical position in the intermediate. We are currently carrying our experiments with labeled ^{13}CO derivatives in order to further elucidate the pathways involved.

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REFERENCES

1 J.W. Faller and A.S. Anderson, *J. Amer. Chem. Soc.*, 92 (1970) 5852.
2 J.W. Faller and A.S. Anderson, *J. Amer. Chem. Soc.*, 91 (1969) 1550.
3 J.W, Faller, A.S. Anderson and C.C. Chen, *J. Organometal. Chem.*, 17 (1969) 7.
4 J.W. Faller, A.S. Anderson and C.C. Chen, *Chem. Commun.*, (1969) 719.
5 A.J. Hart-Davis, C. White and R.J. Mawby, *Inorg. Chim. Acta*, 4 (1970) 431.