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STEREOCHEMISTRY OF SULFUR DIOXIDE AND CARBON MONOXIDE INSERTION REACTIONS OF THREO-1,2-DIDEUTEROPHENETHYL COMPOUNDS OF IRON, MANGANESE AND TUNGSTEN

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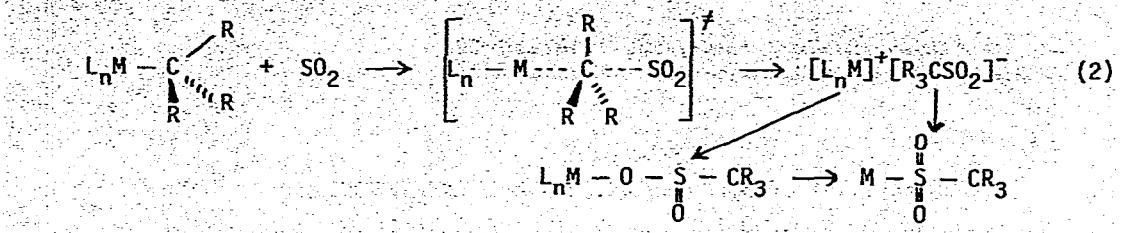
Abstract

Reactions of the compounds threo-PhCHDCHDFe(CO)$_2$(η-C$_5$H$_5$) (I), cis-(threo-PhCHDCHD)Mn(CO)$_4$PEt$_3$ (II) and trans-(threo-PhCHDCHD)W(CO)$_2$(PEt$_3$)(η-C$_5$H$_5$) (III) with SO_2 yield the corresponding S-sulfinates with inversion of configuration, consistent with an S_E2 (inversion) process. Reaction of I with PPh_3 in acetonitrile gives the acyl complex, (threo-PhCHDCHDCO)Fe(CO)(PPh_3)(η-C$_5$H$_5$), consistent with a 1,2-migration of the alkyl group from the metal to a coordinated carbonyl group.

Sulfination of transition metal alkyl compounds (eq. 1) is a very

$$L_nM - R + SO_2 \longrightarrow L_nM - \overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}} - R \qquad (1)$$

general reaction which has been much studied [1]. Although often referred to as an "insertion reaction", because of the nature of the product(s), current opinion actually favours an S_E2 (inversion) [2] type of mechanism (2) [1], i.e.



(2)

The product obtained is generally the S-sulfinate, although O-sulfinate isomers are sometimes detected. Such a mechanism requires inversion of stereochemistry at the α-carbon atom, a phenomenon which has previously been reported for reaction (3) [3]

$$\underline{\text{erythro}}\text{-}Me_3CCHDCHDFe(CO)_2(\eta\text{-}C_5H_5) + SO_2 \longrightarrow \underline{\text{threo}}\text{-}Me_3CCHDCHDSO_2Fe(CO)_2(\eta\text{-}C_5H_5) \quad (3)$$

We have utilized the primary alkyl ligand threo-PhCHDCHD- to study the stereochemistry of a wide variety of alkyl cleavage, transfer and migration reactions [4-7]. We now divulge stereochemical information concerning sulfination reactions of the complexes threo-$PhCHDCHDFe(CO)_2(\eta\text{-}C_5H_5)$ (I), cis-(threo-PhCHDCHD)$Mn(CO)_4PEt_3$ (II) and trans-(threo-PhCHDCHD)$W(CO)_2(PEt_3)(\eta\text{-}C_5H_5)$ (III), as well as the conversion of I to the acyl species, (threo-PhCHDCHDCO)-$Fe(CO)PPh_3(\eta\text{-}C_5H_5)$. The phosphine-substituted compounds, II and III, were chosen over the unsubstituted carbonyl derivatives not only because it was expected that the latter would be much less stable thermally, but also because substitution of a carbonyl group by a tertiary phosphine is known to lead to increased reactivity with SO_2 [1].

Experimental

$^1H\{^2H\}$ and $^{13}C\{^1H\}$ n.m.r. spectra were run on a Bruker HX60 N.M.R. Spectrometer, infrared spectra on a Perkin Elmer 180 instrument and mass spectra on a Jeolco JMS-OISC high resolution mass spectrometer. Analyses were carried out by Microanalysis Laboratories, Ltd., Toronto. Pertinent I.R. and ^1H n.m.r. data are presented in Tables 1 and 2 respectively.

All procedures were performed in vacuo or under a nitrogen atmosphere using Schlenk apparatus. Compound I was prepared as previously reported [6].

Cis-tetracarbonyl(1,2-dideuterophenethyl)(triethylphosphine)manganese(I) (II). The compound $[Mn(CO)_4PEt_3]_2$ was prepared by the method of Lewis et al. [8],

and cleaved with sodium-potassium alloy [9] in THF over nine hours. The resulting solution of $[Mn(CO)_4PEt_3]^-$ was treated with erythro-PhCHDCHDOTs [6] in THF and stirred overnight to give a solution of II. The solvent was removed under reduced pressure, and the product was extracted with petroleum ether (b.p. 30-60°) and then filtered through Celite. The filtrate was cooled to -20° to precipitate any unreacted $[Mn(CO)_4PEt_3]_2$. Further cooling to -78° allowed recovery of unreacted erythro-PhCHDCHDOTs. Finally the orange solution of II was chromatographed on alumina (80-200 mesh) and eluted with 1:1 petroleum ether-benzene. Only the first 75% of the resulting broad yellow band gave pure product, an air-sensitive orange, viscous oil, on removal of solvent under reduced pressure. (Yield 55% based on $[Mn(CO)_4PEt_3]_2$ consumed.)

Trans-dicarbonyl(η-cyclopentadienyl)(1,2-dideuterophenethyl)(triethylphosphine)tungsten(II) (III). The compound cis-$(\eta\text{-}C_5H_5)W(CO)_2(PEt_3)I$, prepared by the method of George and Turnipseed [10], was reduced with sodium-potassium alloy in THF over two hours. The anion solution was then treated with erythro-PhCHDCHDOTs in THF and stirred a further two hours. The THF was removed under reduced pressure and the yellow brown residue was extracted with C_6H_6. After filtering through Celite, the filtrate was concentrated and then chromatographed on alumina (80-200 mesh), a single yellow band being eluted with 1:1 petroleum ether-benzene. Recrystallization of the product from CH_2Cl_2-petroleum ether gave III as yellow needles (yield 78%), m.p. 97 - 99°. Calc. for $C_{21}H_{27}D_2O_2PW$: C, 47.56%; H+D, 5.89%. Found: C, 47.73%; H+D, 5.44%.

Dicarbonyl(η-cyclopentadienyl)(1,2-dideuterophenethylsulfinato)iron(II) (IV). A 0.5 g sample of I was refluxed in neat SO_2 for five hours, after which time the SO_2 was allowed to evaporate. The residue was dissolved in CH_2Cl_2 and chromatographed on an alumina column (80-200 mesh) to yield a small amount of unreacted I. Elution with 1:1 CH_2Cl_2-acetone then gave yellow IV in 75% yield. Calc. for $C_{15}H_{12}D_2FeO_4PS$: C, 51.74%; H+D, 4.62%. Found: C, 51.84%; H+D, 4.36%.

Cis-tetracarbonyl(1,2-dideuterophenethylsulfinato)(triethylphosphine)-manganese(I) (V). A 0.2 - 0.3 g sample of II was refluxed in neat SO_2 for three hours. After allowing the SO_2 to evaporate, the yellow oil was dissolved in CH_2Cl_2 and chromatographed on Florisil, eluting with a 1:1 mixture of CH_2Cl_2 and

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Table 1. Infrared Data (All in petroleum ether unless otherwise stated)

Compound	$\nu(CO)$[a] (cm^{-1})	$\nu(SO)$ (cm^{-1})
threo-PhCHDCHDFe$(CO)_2(\eta\text{-}C_5H_5)$	2012 (s), 1958 (s)	
cis-(threo-PhCHDCHD)Mn$(CO)_4PEt_3$	2053 (m), 1975 (m), 1959 (s), 1935 (m-s)	
trans-(threo-PhCHDCHD)W$(CO)_2(PEt_3)(\eta\text{-}C_5H_5)$	1926 (m), 1846 (s)	
erythro-(PhCHDCHDSO_2)Fe$(CO)_2(\eta\text{-}C_5H_5)$	2040 (m), 1980 (s) (Nujol)	1180 (m), 1035 (m) (Nujol)
cis-(erythro-PhCHDCHDSO_2)Mn$(CO)_4PEt_3$	2087 (m), 2013 (vs), 2002 (s), 1969 (s)	1176 (m), 1040 (m) (liquid film)
trans-(erythro-PhCHDCHDSO_2)W$(CO)_2(PEt_3)(\eta\text{-}C_5H_5)$	1958 (m), 1870 (s) (CH_2Cl_2)	1172 (m), 1032 (m) (Nujol)
threo-PhCHDCHDCOFeCOP$Ph_3(\eta\text{-}C_5H_5)$	1970 (s), 1610 (m)	

a s = strong, m = medium, v = very

Table 2. ^{1}H N.M.R. Data (in $CDCl_3$, TMS internal lock)

Compound [a]	δ(α-CH)	δ(β-CH)	$^3J_{HH}$ (Hz)	Other
threo-PhCHDCHDFe(CO)$_2$(η-C$_5$H$_5$)	1.62	2.65	4.8	δ(Cp) 4.70
cis-(threo-PhCHDCHD)Mn(CO)$_4$PEt$_3$	b	2.84	4.6	δ(CH$_2$) 1.67 (m); δ(CH$_3$) 1.03 (m)
trans-(threo-PhCHDCHD)W(CO)$_2$(PEt$_3$)(η-C$_5$H$_5$)	b	2.81	4.5	δ(Cp) 4.96, J_{PH} ~ 1 Hz; δ(CH$_3$) 1.04 (m); δ(CH$_2$) 1.83 (m)
erythro-(PhCHDCHDSO$_2$)Fe(CO)$_2$(η-C$_5$H$_5$)	3.40	3.24	12.4	δ(Cp) 5.16
cis-(erythro-PhCHDCHDSO$_2$)Mn(CO)$_4$PEt$_3$ [c]	3.35	3.02	12.6	
trans-(erythro-PhCHDCHDSO$_2$)W(CO)$_2$(PEt$_3$)(η-C$_5$H$_5$)	3.43	3.04	12.5	δ(Cp) 5.53, J_{PH} ~ 1 Hz; δ(CH$_3$) 1.07 (m); δ(CH$_2$) 1.94 (m)
threo-PhCHDCHDCOFeCOPPh$_3$(η-C$_5$H$_5$)	2.78, 3.11	2.15, 2.57	5.6	δ(Cp) 4.38, J_{PH} ~ 3 Hz

a All compounds appeared to be diastereomerically pure.

b α-CH resonance obscured by PEt_3 resonances.

c CH_2Cl_2 lock (δ5.35 in SO_2).

acetone. A very narrow yellow band collected between two broad yellow regions was shown by an i.r. spectrum to be the sulfination product, V, in low yield but free of other carbonyl-containing impurities. Other fractions collected contained varying amounts of unknown carbonyl-containing impurities. The product is an air-sensitive orange oil, appearing not to be very robust thermally or photochemically. Calc. for $C_{18}H_{22}D_2MnO_6PS$: C, 47.37%; H+D, 5.74%. Found: C, 47.91%; H+D, 5.71%.

The sample for ^1H n.m.r. spectroscopy was synthesized by condensing ~0.5 ml SO_2, and 0.050 ml CH_2Cl_2 onto 0.08 g of II contained in an n.m.r. tube at -196°. The tube was sealed and allowed to warm to room temperature for 30 minutes before the spectrum of V was taken.

Trans-dicarbonyl(η-cyclopentadienyl)(1,2-dideuterophenethylsulfinato)-(triethylphosphine)tungsten(II) (VI). A 0.2 - 0.3 g sample of III was refluxed in neat SO_2 for two hours, after which time the SO_2 was allowed to evaporate. The yellow oil was dissolved in CH_2Cl_2-Et_2O and formed yellow crystals of VI in 50% yield over five days at -20°. Other preparations which included chromatography on a mina with elution by benzene-acetone mixtures during the work-up procedure yielded a spectroscopically pure product which could not be induced to crystallize. Calc. for $C_{21}H_{27}D_2O_4SPW$: C, 42.44%; H+D, 5.26%. Found for oil: C, 41.68%, H+D, 5.66%.

Carbonyl(η-cyclopentadienyl)(2,3-dideutero-3-phenylpropionyl)(triphenylphosphine)iron(II) (VII). I (0.5 g) was refluxed for six hours under nitrogen in acetonitrile solution (50 ml) with an equivalent amount of PPh_3. The progress of the reaction was monitored by following the growth of the product cyclopentadienyl resonance at δ4.38 ($^3J_{PH}$ = 3 Hz) in the ^1H n.m.r. spectrum. After completion of the reaction, the solvent was removed in vacuo. The product was chromatographed on alumina (80-200 mesh), eluting with 1:1 petroleum ether-methylene chloride. Recrystallization from benzene/petroleum ether yielded the orange-yellow product in 70% yield. Calc. for the perhydro analogue $C_{33}H_{29}FeO_2P$: C, 72.80%; H, 5.34%. Found: C, 73.67%; H, 5.44%.

Discussion

The preparations of compounds I - III are fairly straightforward, and merit little discussion, although II was sufficiently unstable thermally that

good analyses could not be obtained. The formulation of the compound was verified by the mass spectrum of the perhydro analogue (Table 3), in which both the molecular ion and a reasonable fragmentation pattern are evident. The IR spectrum in the carbonyl region is typical of cis complexes of this type [11,12], while the n.m.r. spectrum exhibits reasonable chemical shifts. Integration of the n.m.r. spectrum suggests that the α-CH resonance lies under the methylene resonance of the phosphine.

Formulation of III as the trans isomer is consistent with previous formulations of similar compounds in the literature [10,13], the relative intensities of the carbonyl stretching frequencies and the cyclopentadienyl hydrogen-phosphorus coupling constant being the key data.

Formulation of compounds I - III as the threo diastereomers is based on the low values of $^3J_{HH}$. For purposes of comparison, values of $^3J_{HH}$ for

Table 3. Mass Spectrum of cis-$PhCH_2CH_2Mn(CO)_4PEt_3$

Ion	m/e	Relative Abundance
$[PhCH_2CH_2Mn(CO)_4PEt_3]^+$	390	6
$[PhCH_2CH_2MnCOPEt_3]^+$	306	11
$[PhCH_2CH_2Mn(CO)_4]^+$	285	53
$[PhCH_2CH_2MnPEt_3]^+$	278	8
$[PhMnPEt_3]^+$	250	19
$[Mn(CO)_2PEt_3]^+$	229	19
$[MnCOPEt_3]^+$	201	13
$[HMnPEt_3]^+$	174	100
$[MnPEt_3]^+$	173	53
$[MnC_2H_4Ph]^+$	160	19
$[MnPh]^+$	132	24
$[HPEt_3]^+$	119	42
$[C_2H_4Ph]^+$	105	33
Mn^+	55	68

erythro-I and erythro-II, obtained from epimerized PhCHDCHDI, are 12.6 Hz and 13.5 Hz, respectively. Thus, as expected, all three compounds are formed from erythro-PhCHDCHDOTs with inversion of configuration, consistent with S_N2 attacks by the carbonylate anions on the α-carbon atom of the tosylate [3,4,6,7].

Sulfination of all three alkyl compounds proceeded smoothly and, judging from the sulfur-oxygen stretching frequencies of the products [1], compounds IV - VI, yielded only the S-sulfinates. A large number of compounds analogous to IV are known [1], and IV appears to be quite typical of compounds of the type η-$C_5H_5Fe(CO)_2(SO_2R)$. As previous studies of electrophilic cleavage reactions had demonstrated that some electrophiles induced scrambling of the methylene carbon atoms of I via an intermediate containing a coordinated phenonium ion [6], sulfination of η-$C_5H_5Fe(CO)_2CH_2CH_2Ph$ labelled to the extent of 5% with carbon-13 in the α position [6] was also carried out. Sulfinato product was obtained containing the label intact at the α-position ($\delta(\alpha\text{-}CH_2)$ 73.9, $\delta(\beta\text{-}CH_2)$ 27.8, $\delta(C_5H_5)$ 87.6 ppm with respect to internal TMS), showing that the phenethyl group had behaved as a "normal" alkyl ligand during the reaction.

The manganese and tungsten series, represented here by V and VI, have, however, been much less studied. While compounds of the type $RSO_2Mn(CO)_5$ seem to be quite robust [14], the compound cis-$(MeSO_2)Mn(CO)_4PPh_3$ [15] is unexpectedly labile. Our compound, V, resembles the latter, and could only be characterized with difficulty. It decomposed in the mass spectrometer, but its I.R. and n.m.r. spectra are completely consistent with our formulation.

Although it has been reported that η-$C_5H_5W(CO)_3Me$ in refluxing SO_2 provides only traces of a sulfinato complex [15], η-$C_5H_5Mo(CO)_2(PPh_3)Me$ is much more reactive than is η-$C_5H_5Mo(CO)_3Me$ [1], and thus the observed reaction of our tungsten-alkyl compound, III, is not surprising. Formulation of the product, VI, as the trans isomer is based on the relative intensities of the two I.R. carbonyl stretching bands [13,10] and is consistent with the stereochemistry of the analogous molybdenum series [16].

The relatively large values of $^3J_{HH}$ for the compounds IV - VI (Table 2) show that each of these compounds is the erythro diastereomer. The results are consistent with the one previous stereochemical study of this type [3], and

support the hypothesis that SO_2 "insertion" reactions into transition metal-carbon bonds involve an S_E2 (inversion) process (2). The observed stereospecificity at the metal atoms during the reactions of II and III, on the other hand, is probably not significant. The products, V and VI, assume the thermodynamically more stable configuration [11,17], while Wojcicki et al. [18] have shown that cis-$MeMn(CO)_4(*CO)$ reacts with SO_2 to give both cis and trans products, i.e. in a completely non-stereospecific manner.

Reaction of I with PPh_3 to form the acyl derivative, VII, proceeded with retention of configuration, as expected [3] and consistent with the widely accepted hypothesis that such carbonyl "insertion" reactions actually involve 1,2 migration of the alkyl group, with retention of configuration, to a coordinated carbonyl group [19]. As the central iron atom of VII is chiral, the methylene hydrogens are diastereotopic, as reflected in the ^1H n.m.r. spectrum (Table 2).

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