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A NEW EFFECTIVE METHOD FOR THE RESOLUTION OF PROCHIRAL OLEFINS. STEREOSELECTIVE COORDINATION IN $[PtCl_3(OLEFIN)]^-$ INDUCED BY CRYSTALLIZATION.

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Summary: *Crystallization of $[PtCl_3(olefin)]^-$ $[(\underline{S}-C_6H_5CH(CH_3)N(CH_3)_3]^+$ compounds (olefin = prochiral olefins) affords a single diastereoisomer through a second-order asymmetric transformation.*

The resolution of prochiral olefins through diastereoisomeric complexes containing an asymmetric ligand has been successfully achieved in several cases[1]. These complexes have proved to be interesting model compounds for mechanistic studies on metal-catalyzed olefin activation[2]. In addition they offer the possibility to correlate the absolute configuration of the coordinated olefinic ligand with the sign of the CD-active d-d metal transitions[3]. However the reported resolution methods involve multistep processes and the resulting complexes contain, in most cases, besides the prochiral olefin, another asymmetric ligand in the coordination sphere of the metal.

We report here an extremely simple resolution method affording a diastereoisomeric product containing the olefin as the only asymmetric centre in the metal coordination sphere. The obtained complexes are thus useful starting materials for the synthesis of a variety of enantiomeric complexes of prochiral olefins.

When concentrated aqueous solutions containing a Zeise's type anion $[PtCl_3(olefin)]^-$(olefin = ethene, propene, E-2-butene, 1-butene, styrene)[4] and $(\underline{S})-[C_6H_5CH(CH_3)N(CH_3)_3]Cl$[5] are mixed together at room temperature, a yellow to yellow-orange oil suddenly forms. Careful crystallization of this material from dichloromethane-ethanol mixtures gives an excellent yield (over than 80%) of a single diastereoisomeric ammonium salt $[PtCl_3(olefin)]^-$ $[(C_6H_5CH(CH_3)N(CH_3)_3]^+$, resolved through a second-order asymmetric transformation, *i.e.* the preferential crystallization of one diastereoisomer combined with the re-equilibration in solution through olefin exchange[6]. Some relevant characterization data of these compounds are reported in Table I.

The epimerization half-lives at 20°C and in chloroform solution are of a few minutes for all complexes containing the above reported prochiral olefins, but for the E-2-butene complex. In this case a $t_{\frac{1}{2}}$ of 2 hrs was observed.

Table I. Optical data on $[PtCl_3(olefin)]^-[\underline{S}\text{-}C_6H_5CH(CH_3)N(CH_3)_3]^+$ complexes[a]

Olefin	$[\alpha]_D^{45''}$	$[\alpha]_D^{\infty}$	$[M]_D^{\infty}$
$CH_2{=}CH_2$	- 14.3	- 14.3	- 71
$CH_3CH{=}CH_2$	- 3.5	- 13.6	- 69
$CH_3CH_2CH{=}CH_2$	- 23.5	- 13.9	- 72
$E\text{-}CH_3CH{=}CHCH_3$	+ 3.5	- 13.5	- 70
$C_6H_5CH{=}CH_2$	- 125	- 11.8	- 67

[a] Optical activities were measured at 20°C in $CHCl_3$ solution c = 1.5.

All complexes gave satisfactory elemental analyses and were 1:1 electrolytes.

The absolute configuration of the coordinated E-2-butene in (+) $[PtCl_3(E\text{-}2\text{-}butene)]^-[(\underline{S}\text{-}C_6H_5CH(CH_3)N(CH_3)_3]^+$ was found to be ($\underline{S}$,$\underline{S}$) by the presence of a positive band at 23800 cm^{-1} followed by a negative band at 35000 cm^{-1} in the CD spectrum of this compound recorded in methylcyanide solution[7].

Further work to check the optical purity of the obtained complexes and to assign the absolute configuration to the coordinated prochiral olefins is actually in progress.

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