Simple Organometallic Chiral Derivatising Agents for the ^{31}P N.M.R. Assay of the Enantiomeric Purity of Certain η^2-Donors

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The chiral palladium and platinum ethene complexes (**1**) act as chiral derivatising agents for the ^{31}P n.m.r. assay of the enantiomeric purity of certain chiral alkenes and allenes.

With the heightened interest in asymmetric synthesis that pervades modern organic chemistry, there is a strong demand for further non-chiroptical methods for determining enantiomeric composition. Few such methods exist for assaying chiral alkenes, allenes, or alkynes, although advances have been reported in the application of chiral silver shift reagents,[1] and some work has been carried out with chiral stationary phases for gas chromatography.[2] In seeking a simple n.m.r. method, we have taken advantage of the large chemical shift dispersion of ^{31}P n.m.r.[3] and the relative ease of displacement of ethene by other η^2-donors in organometallic complexes.[4] We report the use of the C_2-symmetric ethene complexes (**1**),[5] for the *in situ* ^{31}P n.m.r. assay of the enantiomeric purity of certain chiral η^2-donors.

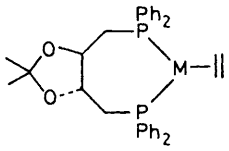
The preparation and simple reactions of the desired (diop)–M^0–C_2H_4† complexes have been reported previously[5] and the complexes may be stored at −20 °C for months without decomposition. The ethene ligand is readily displaced by electron-poor alkenes. Reaction of (**1a**) with a molar excess of the racemic acrylamide (**2**) in [$^2H_6$]benzene led to four distinct AB quartets in the ^{31}P n.m.r. spectrum (with associated platinum satellites) due to the four possible diastereoisomeric species.‡ These are formed by non-selective

† diop is 2,2-dimethyl-4,5-bis(diphenylphosphinomethyl)-1,3-dioxolane.

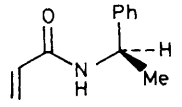
‡ ^{31}P N.m.r. data (C_6D_6, 298 K):

Isomer	δ/p.p.m.		J/Hz		
	P(1)	P(2)	PtP(1)	PtP(2)	P(1)P(2)
(i)	12.8	9.9	3801	3759	57
(ii)	12.7	11.3	3512	3477	61
(iii)	13.6	9.6	3838	3752	57
(iv)	13.3	10.8	3470	3500	64

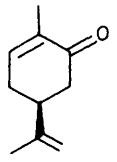
(i) and (ii) [and (iii) and (iv)] are unassigned constitutional isomers related by *Si*- or *Re*-binding of the alkene, while (i) and (iii) [and (ii) and (iv)] are diastereoisomers related by binding of the *S* and *R* enantiomers of (**2**) respectively by the same face.



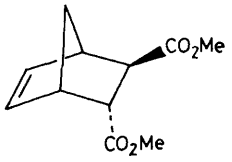
(1) a; M = Pt
b; M = Pd



(2)



(3)



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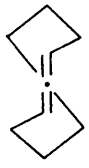
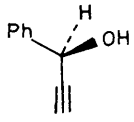


(5)



(6)

binding of the *Si* and *Re* face of both enantiomers. Using the enantiomerically pure *R* and *S* acrylamides, mixtures of known enantiomeric composition were made up and assayed. A linear plot of enantiomeric composition *vs.* ^{31}P n.m.r. measured values was obtained, consistent with no enantioselectivity in binding. Such behaviour may be expected when the chiral centre under examination is remote from the metal centre. Similar behaviour was observed with the diastereoisomeric complexes formed by reaction of (**1a**) and (**1b**) with (*R*)-or (*S*)-5-isopropenyl-2-methylcyclohex-2-enone (carvone), (**3**). In this case, however, the metal is bound with complete stereoselectivity to the less hindered *Si–Si* face of the endocyclic, electron-poor double bond. Typical spectra for the diastereoisomeric platinum complexes are shown in Figure 1, and there was no evidence for selective complexation of one enantiomer. Moreover, the ^{31}P n.m.r. method permits a precise determination of enantiomeric purity. A commercial sample of (−)-carvone (Fluka 22060) was 96% (± 1%) *R*, while the enantiomer (+)-carvone was determined to be >99% *S* (± 0.5%). A sample of (+)-carvone (Koch-Light) of indeterminate age was 86% *S*.

The co-ordinated ethene ligand in (**1**) is also rapidly displaced by addition of allenes and strained alkenes. Excess norbornene reacts with (**1a**) or (**1b**) to give one diastereoisomer [(**b**) $\delta_P(C_6D_6)$ + 6.2 p.p.m., (**a**) δ_P 15.8, J_{PtP} 3414 Hz], consistent with selective complexation of the *exo* face of the double bond. Reaction of (**1a**) with racemic dimethyl *trans*-norbornene-2,3-dicarboxylate (**4**) gave two diastereoisomeric species, precisely in the ratio 50:50. Reaction of (**1a**) with 1,1-dimethylallene gave a single complex (δ_P 18.5, 6.3 p.p.m.; $J_{PtP(1)}$ 3473, $J_{PtP(2)}$ 2842, $J_{P(1)(2)}$ 55 Hz) with preferential binding of the more substituted double bond,[5] while racemic cyclonona-1,2-diene (**5**) was selectively bound by the less-hindered face to give two diastereoisomers in equal ratio [(i) $\delta_{P(1)}$, 17.6, $\delta_{P(2)}$ 11.0 p.p.m., $J_{PtP(1)}$ 3246, $J_{PtP(2)}$ 3057, $J_{P(1)P(2)}$ 71 Hz, (ii) $\delta_{P(1)}$ 17.3, $\delta_{P(2)}$ 10.3 p.p.m., $J_{PtP(1)}$ 3250, $J_{PtP(2)}$ 3060, $J_{P(1)P(2)}$ 71 Hz). Using a literature method for the synthesis of enantiomerically enriched (**5**), a sample was assayed to be 5% *S*.[6]

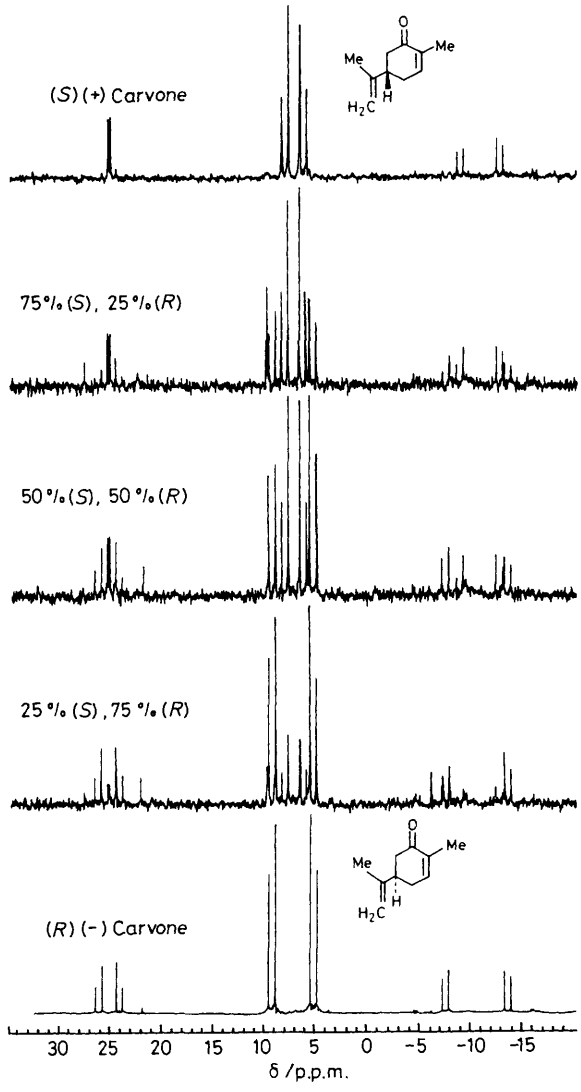


Figure 1. ^{31}P N.m.r. spectra (C_6D_6, 298 K, 101.3 MHz) of the diastereoisomeric complexes formed by reaction of (**1a**) with different samples of carvone of varying enantiomeric composition. Data (C_6D_6, 298 K): [*R*-(**1a**)]-[*S*-(**3**)] $\delta_{P(1)}$ 12.5, $\delta_{P(2)}$ 10.8 p.p.m., $J_{PtP(1)}$ 3409, $J_{PtP(2)}$ 3881, $J_{P(1)P(2)}$ 65 Hz; [*R*-(**1a**)]-[*R*-(**3**)] $\delta_{P(1)}$ 13.8, $\delta_{P(2)}$ 9.9 p.p.m., $J_{PtP(1)}$ 3537, $J_{PtP(2)}$ 3938, $J_{P(1)P(2)}$ 65 Hz.

There are some obvious limitations to this ^{31}P n.m.r. technique. The co-ordinated ethene ligand in (**1**) is not displaced, at room temperature, by excess cyclohexene or cyclopentene or by simple alkyl-substituted ethenes. Furthermore, if the centre of chirality is very close to the metal centre or if a substituent may additionally bind to the metal, then preferred binding of one enantiomer negates the use of this method. For example, the chiral alkyne (**6**) reacted with (**1a**) to give one diastereoisomer only ($\delta_{P(1)}$ 10.8, $\delta_{P(2)}$ 4.6 p.p.m., $J_{P(1)P(2)}$ 33, $J_{PtP(1)}$ 3769, $J_{PtP(2)}$ 3247 Hz). Such behaviour is, of course, well known in studies relating to the mechanism of asymmetric catalysis, involving chiral organopalladium[7] or organorhodium complexes.[8]

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