broader than others. Thus, fractions corresponding to the leading (or trailing) edges are likely enriched in one enantiomer.

Discussion

The data in Table I show that the Bakerbond Chiralcel OD HPLC column is broadly applicable for analytical separations of enantiomers of a variety of chiral neutral organorhenium complexes of the formula $(\eta^5\text{-}C_5R_5)Re(NO)(PAr_3)(X)$. The column derives its chirality from a microcrystalline cellulose urethane, which is coated onto silica.

As has been discussed previously, chromatographic methods offer many advantages for the determination of optical purities.[6] Although commercial columns can be expensive (ca. $1000), subsequent costs are low. In particular, we find the accuracy, precision, and speed of analysis to be superior to that attainable polarimetrically or with chiral NMR shift reagents. Furthermore, the amount of sample needed is extremely low.

Several trends emerge from the data in Table I and Chart I. First, enantiomers of alkyl, aryl, and hydride complexes $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(R)$ (**1**, **2**, **11**, and **13**) separate in all cases. Second, enantiomers of halide and pseudohalide adducts $(\eta^5\text{-}C_5H_5)Re(NO)(PPh_3)(X)$ also separate (**3–6**, **8–10**, **17**). Resolution increases in the series I < Br < Cl ≈ F. Although enantiomers of methoxycarbonyl complex **7** and benzoyl complex **12** separate, those of analogous acetyl and propionyl complexes (**23**, **24**) do not. Similarly, enantiomers of alkynyl complexes **14–16** separate, but those of analogous propynyl and 3,3-dimethylbutynyl complexes (**25**, **26**) do not.

Although the resolution is not exceptional, cyanide complex **17** gives the longest retention time of the compounds examined. Interestingly, the enantiomers of **17** are highly differentiated by the chiral NMR shift reagent $Eu(hfc)_3$.[7] With samples of optically active **17**, these two analytical methods give enantiomer ratios that are in excellent agreement.

Pentamethylcyclopentadienyl complexes $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(X)$ elute much more rapidly than cyclopentadienyl analogues. Although the enantiomers of bromide complex **18** and benzoyl complex **19** separate, enantiomers of other types of complexes resolved in the cyclopentadienyl series do not (**27**, **28**). Note that the resolution observed with **18** and **19** (Table I) is much smaller than that found for cyclopentadienyl analogues **5** and **12**. The tri-*p*-tolylphosphine complexes $(\eta^5\text{-}C_5H_5)Re(NO)(P(p\text{-}tol)_3)(X)$ (**20**, **21**) also elute more rapidly than the PPh_3 analogues. However, enantiomers separate in all cases examined, and the resolution found with cyanide complex **21** is considerably greater than that of PPh_3 analogue **17**.

We are unable to resolve the enantiomers of any carbonyl-substituted complexes $(\eta^5\text{-}C_5R_5)Re(NO)(CO)(X)$ (**29–31**, Chart I part B). We provisionally ascribe this to a requirement for a two-electron donor ligand that is sterically differentiated from NO. However, other explanations are possible. Finally, enantiomers of iron iodide complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)(I)$ (**22**, Chart I part A) separate. However, the resolution is lower than for rhenium analogue **6**, and enantiomers of the corresponding iron methyl complex **32** (Chart I part B) do not separate. Complexes **22** and **32** are, except for a 6–9% contraction in metal–ligand bond lengths, "isosteric" with rhenium analogues **6** and **1**.

We anticipate that significant extensions of the preceding methodology (e.g., related cationic complexes; arene complexes) will be realized in the future, and will report these in our regular research publications.

Experimental Section

Chromatography was conducted on a 10 μM, 4.6 × 250 mm BakerBond Chiracel OD column. Complexes were prepared according to the procedures cited in Chart I. Solvents (EM omnisolve) were filtered through a PALL ultipor N_{66}× 0.45 μm membrane and degassed (sonication, 1 h). The HPLC system consisted of a Waters 590 programmable mobile phase delivery system, a Waters U6K injector, and a Waters lambda-max 481 LC spectrophotometer (set to 280 nm) linked to a HP 3396 integrator. All runs were isocratic.

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(6) See articles collected in: *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1983; Vol. 1 (Analytical Methods).
(7) Dewey, M. A.; Bakke, J. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1349.

Simple Procedure for Conversion of a Trialkyltin Fluoride into the Corresponding Chloride or Bromide

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Summary: Trialkyltin fluorides are converted into the chlorides or bromides on treatment with an excess of the corresponding sodium halide in tetrahydrofuran.

Trialkyltin fluorides are insoluble polymeric solids that can readily be obtained from the chlorides or bromides by shaking these with aqueous alcoholic NaF or KF solutions.[1,2] They have thus been considered to be completely unreactive and therefore useless for synthetic purposes. However, their ready formation has been utilized as a method for removing organotin byproducts formed in organic[3-7] or organometallic[8] syntheses. We now report

(1) Davies, A. G.; Smith, P. J. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1982; Vol. 2, p 550, 552–555.
(2) Tin. *Organotin Fluorides, Triorganotin Chlorides*; Gmehlin Handbuch der Anorganischen Chemie, Part 5; Springer Verlag: Berlin, 1979.
(3) Logue, M. W.; Teng, K. *J. Org. Chem.* **1982**, *47*, 2549.
(4) Kosugi, M.; Suniya, T.; Ogata, T; Sano, H.; Migita T. *Chem. Lett.* 1984, 1225.
(5) Verlhac, J.-B.; Chanson, E.; Jousseaume, B.; Quintard, J.-P. *Tetrahedron Lett.* **1985**, *26*, 6075.

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Table I. Reaction Conditions and Yields for the Conversion of Triorganotin Fluorides into the Corresponding Chlorides or Bromides

R	X	reacn time, days[a]	isolated yield, %[b]
Me	Cl	3	50[c]
Pr	Cl	5	81
Pr	Br	5	48
Bu	Cl	3	65
Bu	Br	5	86
i-Bu	Cl	5	73
Ph	Cl	5	<5
Ph	Br	5	0

[a] At the temperature of refluxing THF. [b] With respect to R_3SnF. [c] Experiment carried out on a 10-mmol scale.

a simple method for reconverting the fluorides to the corresponding chlorides or bromides, thus making possible a recycling of triorganotin reagents. As far as we are aware, there is only one reference to a comparable procedure in the literature: Katsumara[9] was able to convert tributyltin fluoride to the chloride by "treating it with alkali and then with HCl".

Results and Discussion

During the course of this work, we have attempted to convert a number of tri- and diorganotin fluorides into the corresponding chlorides or bromides. We found (see Table I) that this conversion proceeds with good to moderate yields in the case of trialkyltin fluorides when an excess of sodium chloride or bromide is used as the halide source.

$$R_3SnF + NaX \xrightarrow{THF} R_3SnX + NaF$$

X = Cl R = Me, *n*-Pr, *n*-Bu, *i*-Bu

X = Br X = *n*-Pr, *n*-Bu

Triphenyltin fluoride, however, undergoes only ca. 5% conversion to the chloride and does not react under these conditions with sodium bromide. No reaction is observed when sodium halides are replaced by potassium halides, and impure samples of R_3SnF containing traces of KF do not react with the sodium halides. Attempts to extend the conversion to include dialkyltin difluorides were unsuccessful, neither dimethyl- nor dibutyltin difluoride showing any reaction even when 10 equiv of sodium chloride was used.

This apparent disadvantage could in certain circumstances be utilized for the purpose of separating dialkyltin halides from trialkyltin halides; conversion of a mixture of R_3SnX and R_2SnX_2 to the corresponding fluoride mixture followed by treatment with NaX would afford pure R_3SnX.

Various possibilities for optimization of the present procedure come to mind, and three alternatives have been tried for the conversion of tributyltin fluoride to the chloride (potentially the most useful conversion for the synthetic chemist). In each case only one additional variable was introduced: (a) the use of high speed stirring did not accelerate the conversion; (b) addition of the phase-transfer catalyst cetyltribenzylammonium chloride (10 mol % with respect to Bu_3SnF) also had no effect on the reaction rate: (c) the addition of 18-crown-6 (10 mol %) accelerated the reaction and improved the yield somewhat (no catalyst, yield after 72 h = 65%; with catalyst, yield after 48 h = 73%, but yield after 72 h = 75%). However, crown ethers are expensive compared with the other materials required: THF and sodium chloride or bromide are inexpensive and readily available reagents.

Experimental Section

NMR analyses were carried out by using a Bruker AM-300 spectrometer operating at 75.76 MHz for ^{13}C on 50 vol % solutions in $CDCl_3$; GLC analyses, using a Carlo Erba HRGC 5600 instrument (30m DB1 CB quartz column, FID).

For the following experimental procedure to succeed it is necessary that the trialkyltin fluoride be free of KF and water. Repeated washing with water, followed by drying under vacuum, is thus recommended.

The experimental procedure for the conversion is as follows: The trialkyltin fluoride (40 mmol) and the sodium halide (200 mmol) are introduced into a 250-mL round-bottomed flask fitted with a condenser and an argon T-joint. The apparatus is flame-dried, and after cooling, dry THF (150 mL) is added. The mixture is heated at reflux with stirring for 3–5 days. It is then allowed to cool and filtered through a glass filter (diameter 5 cm) containing a layer of silica gel of 1-cm thickness. Filter paper is not suitable.

The solvent is removed with a rotary evaporator and the residue distilled and subjected to GLC and ^{13}C NMR analysis; in each case the purity of the trialkyltin halide is >98%. Boiling points and carbon-13 NMR data[10,11] are in agreement with literature values. In two cases no carbon-13 data appear to have been reported previously: chemical shift values (in ppm vs TMS) are given first, followed by the corresponding coupling constant $^nJ(^{119}Sn,^{13}C)$ (Hz) in parentheses. ^{13}C NMR: Pr_3SnCl 20.14 (n = 1, 341), 18.95 (n = 2, 24), 17.94 (n = 3, 63); *i*-Bu_3SnCl 30.34 (n = 1, 336), 26.24 (n = 2, 21), 26.29 (n = 3, 50).

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(6) Haack, R. A.; Penning, Th. D.; Djuric, S. W.; Dziuba, J. A. *Tetrahedron Lett.* **1988**, *29*, 2783.
(7) Kosugi, M.; Tamura, H.; Sano, H.; Migita, T. *Tetrahedron* **1989**, *45*, 961.
(8) Mitchell, T. N.; Kwetkat, K. *Synthesis* **1990**, 1001.
(9) Katsumara, T. *Nippon Kagaku Zasshi* **1962**, *83*, 724, *Chem. Abs.* **1963**, *59*, 5184.
(10) Mitchell, T. N. *J. Organomet. Chem.* **1973**, *59*, 189.
(11) Nádvornik, M.; Holecek, J.; Handlir, K.; Lycka, A. *J. Organomet. Chem.* **1984**, *275*, 43.