Purification of Organometallic Ligands

with the CombiFlash® EZ Prep

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Chromatography Application Note AN108

Abstract

Organometallic chemistry is, to a large extent, the synthesis and purification of the ligands that are coordinated to the metal at the last stages of synthesizing the ligand-metal complex. CombiFlash systems work well to purify the desired ligand from starting compounds and side-products.

In this application note, a 1,4-diazabutadiene compound is synthesized and purified using a CombiFlash EZ Prep and RediSep Rf Gold® C18 flash columns while using a CombiFlash PurIon L mass spectrometer for detection.

Overview

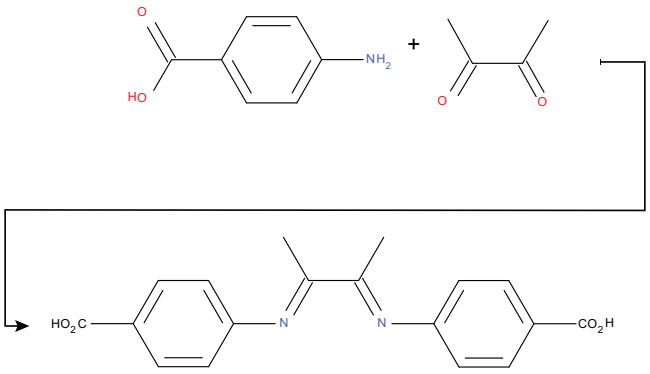
Complexes containing 1,4-diazabutadiene ligands have received attention due to their utility as polymerization catalysts[1]. In this application note, 4-[3-(4-carboxyphenyl)iminobutan-2-ylideneamino]benzoic acid (Figure 1) was synthesized and purified as a model for other ligands. The synthesis of ligands for organometallic compounds is primarily organic synthesis, an area where CombiFlash systems excel in purification.

After synthesis and purification, this ligand can be reacted with either $PtCl_2$ or $PdCl_2$ to form the final complex in the cited paper[2].

Experimental and Results

Starting compounds were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Chromatography solvents were purchased from VWR (Radnor, PA, USA).

The synthesis of 4-[3-(4-carboxyphenyl)iminobutan-2-ylideneamino]benzoic acid was performed according to a published procedure[2]. Briefly, 1,4-aminobenzoic acid (2.9 g, 21 mmol) was dissolved in dry methanol (10 mL) to which 4 drops of formic acid was added. This was followed by the droplet addition of 2,3-butanedione (0.9 mL, 10 mmol). The mixture was stirred overnight at room temperature.



Formula Weight : 324.3
Exact Mass : 324.1
Formula : $C_{18}H_{16}N_2O_4$

Figure 1: Synthesis of 4-[3-(4-carboxyphenyl)iminobutan-2-ylideneamino]benzoic acid

The mixture was evaporated to dryness. A small amount (< 1 mg) was dissolved in 20 mL of tetrahydrofuran (THF) and injected onto the CombiFlash PurIon L mass spectrometer to determine that the desired compound was produced as shown in Figure 2.

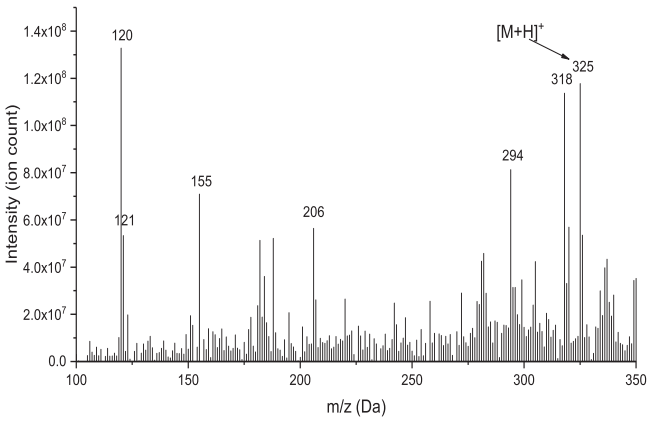


Figure 2: Mass spectrum of crude 4-[3-(4-carboxyphenyl)iminobutan-2-ylideneamino]benzoic acid which shows an $[M+1]^+$ peak at 325 Da

The purification of the diazabutadiene ligand used a RediSep Rf Gold C18 flash column (PN 69-2203-336). A sample (0.2015 g) was dissolved in 2 mL of dimethyl sulfoxide (DMSO) and run according to the gradient in Figure 3. UV detection was at 214 and 254 nm. The

solvent system was water/THF both containing 0.1% formic acid. This solvent system was chosen because the desired compound is soluble in THF. The CombiFlash PurIon L was set to 325 Da. The time scale was programmed for column volumes (CV) to allow for easy scale-up to larger columns. The ligand didn't absorb at the chosen wavelengths, but it was easily collected by mass-directed fractionation.

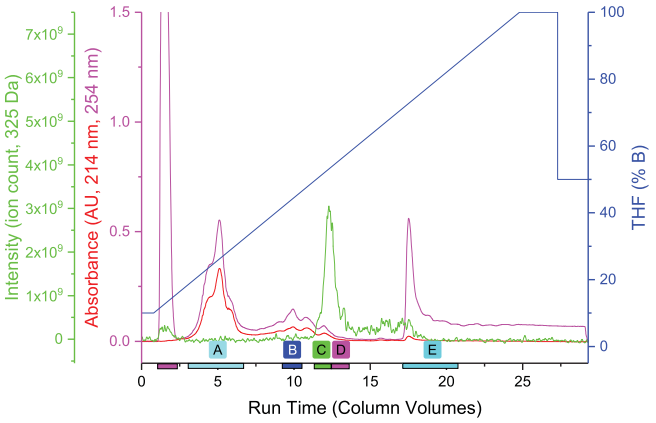


Figure 3: Purification of a diazabutadiene ligand using mass directed fractionation

Table 1: Results

Collection Time (CV)	Mass Recovered (mg)
3.4-6.9 A	104.3
9.5-10.6 B	27.8
11.7-13.2 C D	16.0
17.2-20.7 E	7.7
Total:	**155.8 (77% recovery)**

The peak visible from 1.1-2.5 column volumes was the DMSO used to inject the sample. The flash column provided sufficient resolution to purify the ligand, but the purification could be performed with preparative HPLC column on the CombiFlash EZ Prep if necessary.

Conclusion

The CombiFlash EZ Prep purification system coupled with the CombiFlash PurIon L mass spectrometer detector is a powerful combination for the purification of compounds. The combination of UV and mass directed fractionation ensures the desired compound is collected, even if it doesn't absorb at the wavelengths selected for purification. The mass spectrometer can be used as a specific detector using a specific mass ion for collection. This system works well for purifying ligands prior to coupling to metals to form the final product.

[1] Ittel, S.D; Johnson, L.K.; Brookhart, M. *Chem. Rev.* Late-Metal Catalysts for Ethylene Homo- and Copolymerization. **2000**, *100*, 1169-1203

[2] Buffin, B.P.; Kundu, A. Synthesis, characterization, and crystal structure of platinum(II) and palladium(II) chlorides with an acidic α-diimine ligand. *Inorg. Chem. Commun.* **2003**, *6*, 680-684

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