

### Solvates: Avoiding Common Errors

Special care that must be taken in characterizing compounds that crystallize as solvates. An experimental procedure from a thesis is given below. The purpose of this handout is to critique several misleading features.

$[(\eta^5\text{-C}_5\text{H}_5)\text{Re}(\text{NO})(\text{PPh}_3)(=\text{CHCH}_3)]^+ \text{PF}_6^-$  (**25**). A solution of **18** (0.314 g, 0.549 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was cooled to  $-78^\circ\text{C}$ . Then solid  $\text{Ph}_3\text{C}^+ \text{PF}_6^-$  (0.234 g, 0.604 mmol) was added with stirring. After 30 min, the cold bath was removed. After 1 h, hexanes (15 mL) was added. The solvent was removed by oil pump vacuum. The off-white powder was collected by filtration and washed with hexanes followed by several small portions of  $\text{Et}_2\text{O}$ . The sample was dissolved in  $\text{CHCl}_3/\text{CH}_2\text{Cl}_2$ , and  $\text{Et}_2\text{O}$  was slowly added by vapor diffusion. After 2 days, greenish yellow leaflets of **25** (0.311 g, 0.434 mmol, 79%) were collected by filtration, mp  $165^\circ\text{C}$  dec. IR ( $\text{cm}^{-1}$ ,  $\text{CH}_2\text{Cl}_2$ ):  $\nu_{\text{NO}}$  1720 s;  $^1\text{H}$  NMR ( $\delta$ ,  $\text{CD}_2\text{Cl}_2$ ): 15.82 (ReCH, q,  $J = 8.0$  Hz, 1H), 7.62-7.28 (phenyl, m, 15H), 5.94 ( $\text{C}_5\text{H}_5$ , s, 5H), 2.53 ( $\text{CH}_3$ , d,  $J = 8.0$  Hz, 3H);  $^{13}\text{C}$  NMR (ppm, acetone- $d_6$ ): 310.7 (br s), 133.8 (d,  $J = 11.9$  Hz), 133.0, 130.6 (d,  $J = 32.3$  Hz), 130.1 (d,  $J = 10.9$  Hz), 100.7 ( $\text{C}_5\text{H}_5$ ), 44.0 ( $\text{CH}_3$ ). Anal. Calcd. for  $\text{C}_{25}\text{H}_{24}\text{F}_6\text{NOP}_2\text{Re}$ : C, 41.91; H, 3.38; N, 1.95; P, 8.63; Calcd. for  $\text{25}\cdot(\text{CHCl}_3)_{0.5}$ : C, 39.30; H, 3.16; N, 1.79; P, 7.93; Found: C, 39.59; H, 3.35; N, 1.73; P, 7.68.

(1) The isolation of "greenish yellow leaflets" of the ethylidene complex "**25**" is claimed. However, upon further reading, this material is noted (?) to be a  $\text{CHCl}_3$  solvate. Therefore, the final sentence should read:

After 2 days, greenish yellow leaflets of  $\text{25}\cdot(\text{CHCl}_3)_{0.5}$  (0.311 g, 0.434 mmol, 79%) were collected by filtration, mp  $165^\circ\text{C}$  dec.

(2) The yield is incorrectly calculated. The formula weight of **25** is ca. 716, whereas that of  $\text{25}\cdot(\text{CHCl}_3)_{0.5}$  is 776. The former value was used to calculate the yield, but the latter material was isolated. Therefore the yield is erroneously high. Corrected version:

After 2 days, greenish yellow leaflets of  $\text{25}\cdot(\text{CHCl}_3)_{0.5}$  (0.311 g, 0.401 mmol, 73%) were collected by filtration, mp  $165^\circ\text{C}$  dec.

(3) The only datum supporting the existence of the solvate is a partial elemental analysis. There is no direct evidence, such as (1) observation of the solvate by NMR, or (2) chlorine analysis. A reader might suspect that the researcher hadn't bothered to check for a solvate, submitted the sample for analysis, and then obtained an analysis that did not fit the formula. The analysis was then "retrofit" to a solvate. This is poor technique. Someone who wishes to repeat this work really has no idea of what was really isolated. The following protocol would prevent this from occurring.

(3.1) After obtaining crystals, run a NMR spectrum in a solvent other than the recrystallization solvent(s) to see if any solvate is present. If a solvate is present, integrate (or add an internal standard) to determine the amount. Some solvates will be difficult to detect by  $^1\text{H}$  NMR (e.g.,  $\text{CHCl}_3$  in the presence of  $\text{PPh}_3$ ). In these cases, a  $^{13}\text{C}$  NMR assay could be used. The solvate signals should be included in the NMR data reported in the experimental.

(3.2) Determine how "tight" the solvate is. Does it come off *in vacuo* (drying pistol)? Is it retained after several weeks on the bench? This should be part of the experimental.

(3.3) If your solvate contains -Cl, request chlorine analysis. The solvent quantity determined by microanalysis should agree with that determined by NMR.

(3.4) Other points:

(3.4.1) If you have isolated a solvate, it may save you work to change your isolation conditions to obtain a non-solvated material. Diffusion recrystallization conditions often give solvates (and three-solvent systems such as in this example should be avoided).

(3.4.2) If you are using a non-solvate, but only the solvate has been reported in the literature (or vice-versa), then you are using a new, previously uncharacterized form of matter. There is no need to repeat solution spectra, but you must put your new isolation procedure in the literature, and establish the purity of your new material (microanalysis)

(3.4.3) Avoid at all times "fantasy solvates". This is a compound that did pass microanalysis, and for which a "solvate" was invented, *with no independent supporting evidence*, in order to make the microanalysis fit.