Preliminary communication

APPLICATION OF SIZE EXCLUSION CHROMATOGRAPH (SEC) TO ORGANOMETALLIC COMPOUNDS

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Summary

The utility of modern size-exclusion chromatography for the separation and identification of organometallic compounds is described with examples from studies on low-valent complexes of nickel and iron.

High performance liquid chromatography (HPLC) is a powerful analytical *tool* which is finding increasing acceptance among organometallic chemists [1—5]. More widespread use has been impeded by two major factors. First, the large number of chromatographic variables to be adjusted for each new sample requires a considerable investment in time and effort. Second, many organometallics are unstable to the chromatographic process, i.e., adsorption on silica or alumina, or the use of water in reversed-phase chromatography. A relatively new HPLC technique, size-exclusion chromatography (SEC) overcomes these difficulties. Here we describe the use of SEC in our work with low-valent nickel and iron complexes.

SEC uses a porous, inert packing to separate compounds on the basis of molecular size, with larger molecules eluting first [6]. Since the separation is based on size, chemically different compounds can often be determined without adjusting the chromatographic conditions. The mechanism is very gentle, involving only the differential diffusion of sample molecules into the solvent-filled pores. Retention can be related to the molecular size by chromatographing standards and constructing a calibration curve [6].

For this work, SEC provided the opportunity to work with a wide range of metal—ligand systems with very little time spent on method development. The inherently gentle mechanism, the use of a nitrogen-flushed solvent and a packing with no reactive oxygens (a polystyrene-divinylbenzene resin) allowed us to chromatograph fairly reactive and air-sensitive compounds. With

continuous monitoring of the column effluent, qualitative and quantitative information can be obtained in a single experiment. The retention volume is a function of molecular size and the peak height (or area) can be calibrated to yield the concentration of a component. The use of small (~10 μm) particles has greatly improved the speed and efficiency of SEC [7]. In our studies every separation was completed in twelve minutes, regardless of the sample used.

The chromatographic conditions are summarized below: Instrument: Du Pont 820 liquid chromatograph; Injection: 25 μl; Valco sampling valve, Model CV-6-UHPa-N60; Columns: Waters 100 Å μ-Styragel columns in series (120 cm total length); Detection: Du Pont 254 nm UV photometer and Du Pont differential refractometer; Solvent: Burdick and Jackson "distilled in glass" tetrahydrofuran; Sample concentration: Average 1% (w/v) in solvent; Pressure: 2760 psi (19 MPa); Flow: 3.6 ml/min.

UV grade tetrahydrofuran was used because the butylated hydroxytoluene (BHT) added to other grades of tetrahydrofuran can interfere with detection. All samples were filtered before injection in an inert-atmosphere dry box using 0.2 μm Fluoropore filters (Millipore Corporation).

Figure 1 shows the molecular weight (Mw) vs. retention volume (V_R) calibration obtained with a series of ligands and nickel(0) complexes. The data are presented in Table 1. The NiL_4 complexes are known to be undissociated in solution [8]. The solid line on the graph is the calibration curve for this column set obtained with known molecular weight polystyrene (PS) standards. Molecular weight is often used as an approximation of molecular size [6]. Despite the obvious structural differences between the random-coil polystyrene
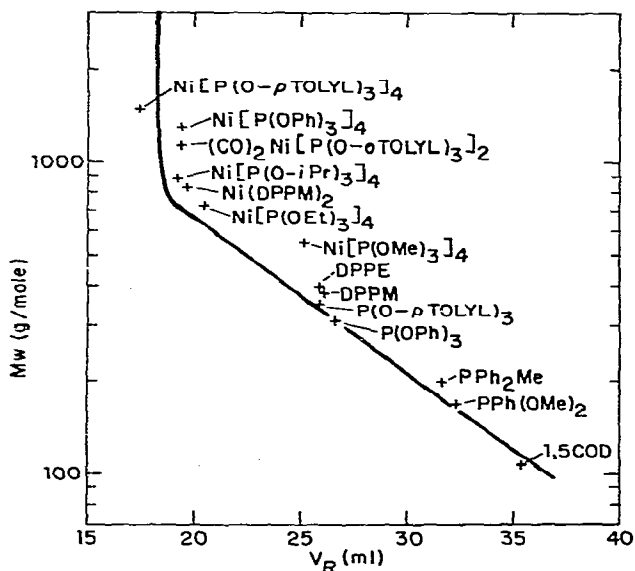

Fig. 1. Molecular weight (Mw) versus retention volume (V_R) for nickel complexes and free ligands. The solid line is a polystyrene (PS) calibration. For experimental conditions, see text. (Ph = phenyl; 1,5-COD = 1,5-cyclooctadiene; DPPM = Bis(diphenylphosphino)methane; DPPE = Bis(diphenylphosphino)ethane).

TABLE 1

SEC DATA FOR COMPOUNDS STUDIED

	Mol.wt. (g/mol)	V_R (ml)
Ni[P(O-p-Tolyl)$_3$]$_4$	1467	17.4
Ni[P(OPh)$_3$]$_4$	1299	19.4
(CO)$_2$Ni[P(O-o-Tolyl)$_3$]$_2$	1143	19.4
Ni[P(O-i-Pr)$_3$]$_4$	891	19.2
Ni(DPPM)$_2$	827	19.6
Ni[P(OEt)$_3$]$_4$	723	20.5
Ni[P(OMe)$_3$]$_4$	555	25.2
DPPE	398	25.9
DPPM	384	26.1
P(O-p-Tolyl)$_3$	352	25.8
P(OPh)$_3$	310	26.6
PPh$_2$Me	200	31.7
PPh(OMe)$_2$	170	32.3
1,5-COD	108	35.4
"Fe[P(O-p-Tolyl)$_3$]$_4$"	1462	18.8
"Fe[P(OPh)$_3$)$_4$"	1294	19.6
HFeCl(DPPE)$_2$	888	22.6
H$_2$Fe(DPPE)$_2$	854	21.9
(COD)Fe[P(O-i-Pr)$_3$]$_3$	788	21.6
(COD)Fe[P(OEt)$_3$]$_3$	662	22.4
(COD)Fe[P(OMe)$_3$]$_3$	536	25.8
Fe(PF$_3$)(DMPE)$_2$	444	27.6
FeCl$_2$(DMPE)$_2$	427	28.6
Fe(CO)(DMPE)$_2$	384	27.3

polymer and the almost spherical organometallic complexes, Fig. 1 shows a relatively close fit of the data.

Figure 2 shows the superimposition of three single-component chromatograms illustrating the efficiency of SEC over the molecular weight range covered.

The results of experiments with a series of iron complexes are plotted in Fig. 3 and listed in Table 1. These compounds are displaced from the polystyrene calibration curve, included on the graph, and also from the nickel data. The retention of (COD)Fe[P(OR)$_3$]$_3$ complexes [9] shows the expected dependence on the nature of R. It is clear from this work that complexes differing in the number of ligands can be readily separated by SEC. Difficulties may be expected in separating isomers or complexes differing only in the central metal or in small ligands (for example Fe(CO)(DMPE)$_2$ and FeCl$_2$(DMPE$_2$) [10,11]. Also although H$_2$Fe(DPPE)$_2$ occurs in two crystalline forms [12], these species cannot be separated by SEC, since they behave identically in solution. In general, separation by SEC requires about 10% difference in the solvated molecular size of the compounds.

SEC played an important role in clarifying the structure of "Fe[P(OPh)$_3$]$_4$" (A). Initial ^{31}P{^{1}H} studies at 36.43 MHz of the product from the reaction [13] of P(OPh)$_3$ and Fe(COD)$_2$ gave a very complex and non-interpretable pattern. This raised serious questions about the nature and purity of the sample. The SEC analysis showed a single peak with the same retention volume as Ni[P(OPh)$_3$]$_4$, providing evidence of purity and confirmation of the
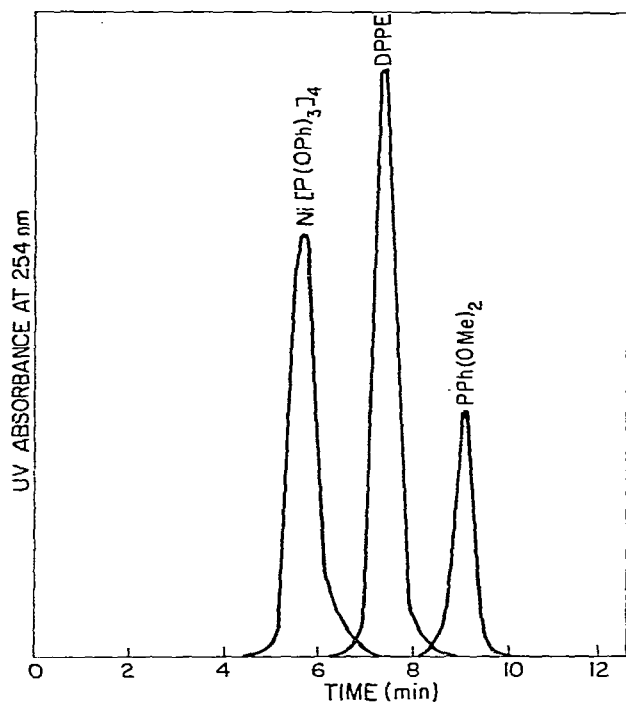
Fig.2. Superimposed chromatograms. UV detector only. For experimental conditions, see text.
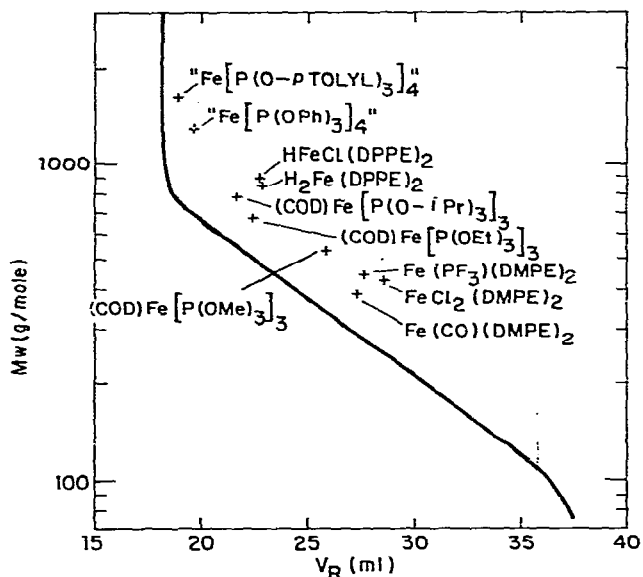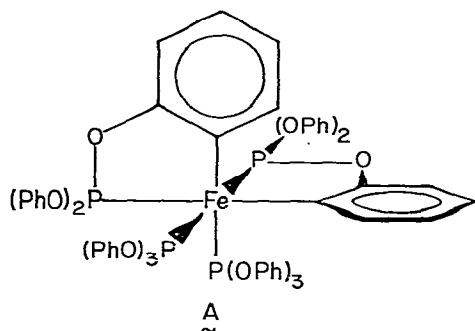

Fig.3. Molecular weight (Mw) versus retention volume V_R for Fe complexes. Solid line is PS calibration. For experimental conditions, see text. (COD = 1,3-cyclooctadiene). The quotation marks on "Fe[P(O-p-tolyl)$_3$]$_4$" and "Fe[P(OPh)$_3$]$_4$" indicate that the structures are not simple tetrahedra. See A.

expected molecular size. Later ^{31}P spectra at 109.3 MHz (obtained with a superconducting magnet) confirmed the purity of the complex and the ABCD spin system. We found the same retention volume for the structurally analogous "Ru[P(OPh)$_3$]$_4$" [13].

While careful sample handling and purging the solvent with N$_2$ made studying moderately air-sensitive compounds possible, these precautions were still not sufficient for very air-sensitive compounds such as Ni(PMe$_3$)$_4$ (pyrophoric), Ni[P(O-o-tolyl)$_3$]$_3$ or HFeNp(DMPE)$_2$ [11,12], (Np = 2-naphthyl). With these compounds only peaks corresponding to the free ligands were found. In the last two cases, the difficulty was circumvented by prior treatment of the solutions with CO. This gave the less air-sensitive (CO)$_2$Ni[P(O-o-tolyl)$_3$]$_2$ and (CO)Fe(DMPE)$_2$ which were readily identified by SEC retention and IR spectra.

Larger pore-size columns provide resolution of higher molecular weight complexes. Further study on the separation of extremely air-sensitive compounds will explore the use of silica-based packings [14] which are compatible with a wide variety of solvents with low affinity for oxygen.

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