Dispersion Polymerizations in Supercritical Carbon Dioxide

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Conventional heterogeneous dispersion polymerizations of unsaturated monomers are performed in either aqueous or organic dispersing media with the addition of interfacially active agents to stabilize the colloidal dispersion that forms. Successful stabilization of the polymer colloid during polymerization results in the formation of high molar mass polymers with high rates of polymerization. An environmentally responsible alternative to aqueous and organic dispersing media for heterogeneous dispersion polymerizations is described in which supercritical carbon dioxide (CO_2) is used in conjunction with molecularly engineered free radical initiators and amphipathic molecules that are specifically designed to be interfacially active in CO_2. Conventional lipophilic monomers, exemplified by methyl methacrylate, can be quantitatively (>90 percent) polymerized heterogeneously to very high degrees of polymerization (>3000) in supercritical CO_2 in the presence of an added stabilizer to form kinetically stable dispersions that result in micrometer-sized particles with a narrow size distribution.

Table 1. Results of MMA polymerizations with F-AIBN and AIBN as the initiator in CO_2 at 204 bar and 65°C (*22*); stabilizer is either LMW or HMW poly(FOA). MWD, molecular weight distribution.

Stabilizer (w/v %)	Yield (%)	$<M_n>$ (10^3 g/mol)	MWD	Particle size (μm)
		F-AIBN		
0%	10	77	2.9	
2% LMW	98	277	2.5	2.0 (±0.2)
4% LMW	91	303	2.3	0.9 (±0.3)
1% HMW	38	163	2.3	
2% HMW	47	193	2.3	2.4 (±0.2)
4% HMW	74	281	2.5	1.4 (±0.1)
		AIBN		
0%	39	149	2.8	
2% LMW	85	308	2.3	1.2 (±0.3)
4% LMW	92	220	2.6	1.3 (±0.4)
2% HMW	92	315	2.1	2.7 (±0.1)
4% HMW	95	321	2.2	2.5 (±0.2)

The dissemination of volatile organic compounds, chlorofluorocarbons, and aqueous-waste streams into our environment has prompted considerable worldwide concern, and environmental issues are now of paramount interest to the chemical industry. To survive, the chemical industry must be able to conform to more environmentally sound practices in the manufacture and processing of products. Herein, we describe the use of supercritical CO_2 as a dispersing medium for the manufacture (and processing) of polymeric materials. Specifically, we have developed a dispersion polymerization process in which polymeric stabilizers, molecularly engineered to be interfacially active in CO_2, are used to form a stable polymer colloid consisting of a lipophilic dispersed phase in a CO_2 continuous phase. This procedure allows for the synthesis of high molar mass acrylic polymers in the form of micrometer-sized particles with a narrow size distribution.

This polymerization methodology obviates the use of aqueous and organic dispersing media in this classical manufacturing route to many of the polymers made on a large commercial scale such as polystyrene, poly(alkyl acrylate)s, poly(ethylene-*co*-vinyl acetate), poly(vinyl chloride) (PVC), styrene-butadiene rubber, acrylonitrile-butadiene-styrene terpolymers, poly(acrylic acid), and poly(acrylamide) (*1*). Typically, these polymers are synthesized with either water (for water-insoluble polymers) or an organic solvent (for water-soluble polymers) used as the dispersing medium. Such heterogeneous polymerizations usually form at least two phases in which the starting monomers or the resulting polymer, or both, are in the form of a fine dispersion in an immiscible liquid phase; particle sizes typically range from 50 nm to several millimeters and can be controlled with surfactants to within a relatively narrow size distribution. There are basically four different heterogeneous polymerization techniques—precipitation, suspension, emulsion, and dispersion processes—which are distinguished by (i) the initial phase behavior of the polymerization mixture, (ii) the polymerization kinetics, and (iii) the mechanism of particle formation (*2*).

This report focuses on the design of a dispersion polymerization in supercritical CO_2. Typically, a free radical dispersion polymerization starts as a one-phase, homogeneous system such that both the monomer and the polymerization initiator are soluble in the polymerization medium but the resulting polymer is not (*3, 4*). As a result, the polymerization is initiated homogeneously and the resulting polymer phase separates into primary particles. Once nucleated, these primary particles become stabilized by amphipathic molecules present in the system that prevent particle flocculation and aggregation. Polymer colloids produced by dispersion polymerizations are usually stabilized by a "steric" mechanism as compared with an electrostatic mechanism that is common to colloidal stabilization in aqueous environments (*3–7*). Steric stabilization of a colloidal dispersion is usually imparted by amphipathic macromolecules that become adsorbed onto the surface of the dispersed phase. These amphipathic macromolecules contain an anchoring segment, which attaches to the particle usually by physical adsorption, and stabilizing moieties that are soluble in the continuous phase. The stabilizing moieties project into the continuous phase (which needs to be a good solvent for the stabilizing moieties) and prevent flocculation by mutual excluded volume repul-

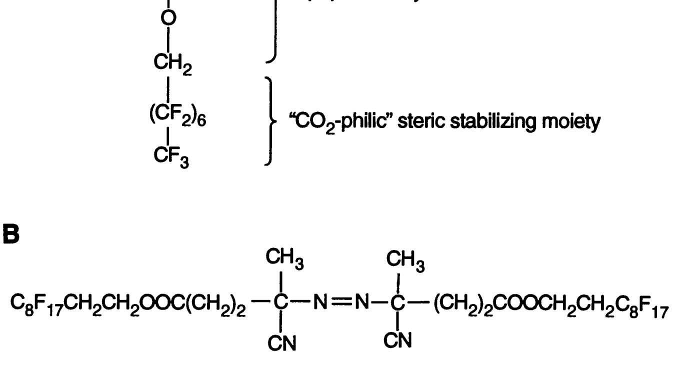

Fig. 1. The chemical structures of (**A**) an interfacially active, polymeric stabilizer [poly(FOA)], depicting the proposed site of anchorage for the CO_2-philic steric stabilizing moieties, and (**B**) a free radical initiator (F-AIBN) that has the solubility characteristics to selectively partition into a supercritical CO_2 phase over either a hydrophilic dispersed or a lipophilic dispersed phase.

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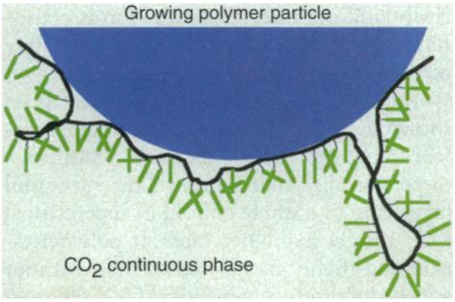
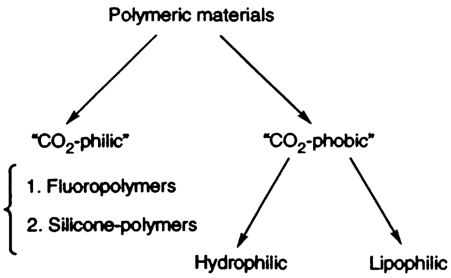


Fig. 2. Schematic illustration of a PMMA particle (shown in blue) stabilized by poly(FOA) in which the lipophilic backbone (shown in black) acts as an anchor for the fluorocarbon steric-stabilizing moieties (shown in green).

sions during a Brownian collision, thereby imparting stability to the colloid.

Recently, we successfully synthesized high molar mass fluoropolymers using homogeneous free radical polymerization methods in supercritical CO_2 (*8–12*). However, most high molar mass polymers are not soluble to any appreciable extent in supercritical CO_2—fluoropolymers and silicones are exceptions. Therefore, alternative processes are necessary to take advantage of this solvent alternative for the synthesis (and processing) of conventional, hydrocarbon-based polymers that do not have significant solubility (tens of percent) in supercritical CO_2 at relatively "mild" conditions (temperatures $T < 100°C$, pressures $P < 350$ bar). On the basis of experimental observations of the solubilities of materials in CO_2 (*8, 10–19*), we can therefore categorize polymeric materials as being either "CO_2-philic" (*19*) or "CO_2-phobic" materials; by these criteria, amorphous fluoropolymers and silicone-polymers essentially define CO_2-philic (Scheme 1). This categorization dictates the design parameters of an interfacially active molecule for CO_2: It requires the intramolecular combination of a CO_2-philic segment (stabilizing moiety) with a CO_2-phobic segment (anchor). The CO_2-phobic segment can be either hydrophilic or lipophilic depending on the nature of the dispersed phase that is to be stabilized.

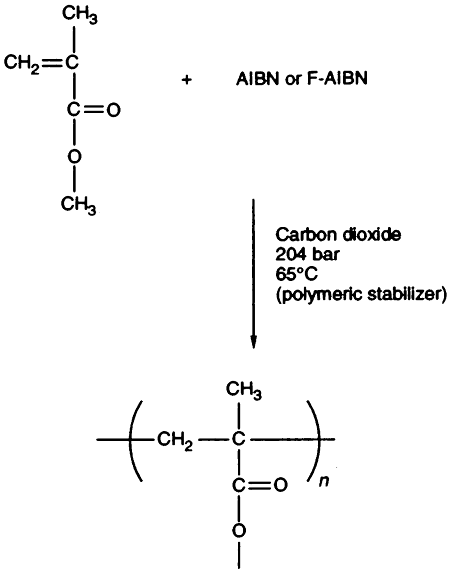


Scheme 1. Categorization of the solubility of polymeric materials in supercritical CO_2, which establishes the guidelines for the molecular engineering of amphipathic molecules in analogy to the hydrophile-lipophile balance concept used for the description of conventional surfactants.

One class of amphipathic materials that meet the criteria for a stabilizer for the polymerization of lipophilic monomers such as methyl methacrylate (MMA) is based on poly(1,1-dihydroperfluorooctylacrylate) [poly(FOA)] (Fig. 1A). The CO_2-philic fluorocarbon segment extends the poly(FOA) chain trajectory into the continuous phase, thereby preventing flocculation of particles through a steric stabilization mechanism. The lipophilic acrylic backbone will preferentially adsorb onto an acrylic colloidal particle, providing a surface anchor for the CO_2-philic fluorocarbon stabilizing moieties (see Fig. 2) (*5*). As described earlier (*8*), this polymeric stabilizer can itself be readily synthesized (homogeneously) in CO_2 (*20*).

We have also designed a free radical polymerization initiator that can partition itself into the continuous CO_2 phase versus either a lipophilic dispersed phase or a hydrophilic dispersed phase (Fig. 1B). This highly fluorinated initiator (F-AIBN), made by treating 4,4′-azobis-4-cyanopentanoyl chloride with 1,1,2,2-tetrahydroperfluorodecanol, is highly soluble in CO_2, and its decomposition is analogous to that of 2,2′-azobis(isobutyronitrile) (AIBN) (*9*).

Polymerizations of MMA were conducted in supercritical CO_2, with and without added stabilizer; in these polymerizations either F-AIBN or AIBN was used as the free-radical initiator (see Scheme 2). The high-pressure polymerizations were carried out in a view cell equipped with sapphire windows (*8*) to visually verify the phase behavior during the polymerization. For a typical polymerization, the initiator (4×10^{-5} mol of either AIBN or F-AIBN) and the polymeric stabilizer [poly(FOA)] were placed into a 10-ml high-pressure reaction view cell containing a magnetic stir bar. The cell was purged with argon for 10 min, and the monomer (2 g of MMA, purified by column chromatography) was injected into the cell under an argon atmosphere. The cell was then filled with CO_2 to ~70 bar with an Isco syringe pump. While the cell was heating to 65°C, the pressure was gradually increased to 204 (±0.5) bar by the addition of more CO_2. The system was maintained at these conditions for 4 hours, and then the reactor was cooled and the CO_2 was vented. Johnston and co-workers have recently shown that the glass transition temperature of poly(methyl methacrylate) (PMMA) decreases with an increase in CO_2 pressure as a result of solvent swelling (plasticization) of the polymer (*21*). Therefore, under the conditions used for our investigations the reaction temperature is above the glass transition temperature of the highly plasticized PMMA particles. This circumstance should facilitate the rate of monomer diffusion into the growing polymer particles. Furthermore, such plasticization points to the potential for synthesizing new (composite) materials through the introduction of a second component (monomer, polymer, dye, pharmaceutical agent) into the swollen particle that may not be accessible with the use of conventional heterogeneous polymerization methods.



Scheme 2. Synthesis of poly(methyl methacrylate) with a dispersion polymerization method in supercritical CO_2.

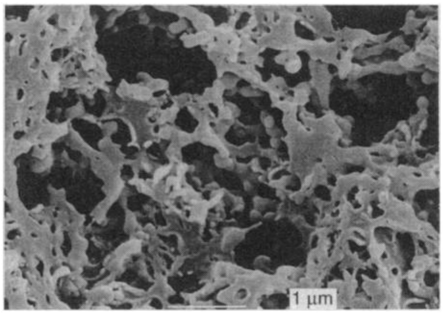


Fig. 3. Scanning electron micrograph of PMMA synthesized in CO_2 without stabilizer.

The data on polymerizations of MMA in supercritical CO_2 with and without added stabilizer are summarized in Table 1 (*22*). Two different stabilizers were used: a low molecular weight (LMW) poly(FOA) (number-averaged molar mass $\langle M_n \rangle = 1.1 \times 10^4$ g/mol) and a high molecular weight (HMW) poly(FOA) ($\langle M_n \rangle = 2.0 \times 10^5$ g/mol) (*23*). All polymerizations were initially homogeneous, as MMA monomer is soluble in CO_2 at the reaction conditions utilized. In the absence of stabilizer [that is, 0% (w/v)] for both initiators (F-AIBN and AIBN), the resultant PMMA accumulated as a thick irregular film on the interior walls and windows of the view cell, clearly indicative of a precipitation reaction. These precipitation polymerizations of MMA conducted without stabilizer were unsuccessful as the reactions were found to proceed only to low conversions and resulted in polymer with relatively low molar masses (see Table 1). Scanning electron microscopy (SEM) was also used to determine the morphology of the PMMA that formed in supercritical CO_2. Without added stabilizer, a nondescript morphology was observed for these precipitated, unstabilized particles (Fig. 3).

In remarkable contrast, the dispersion polymerization of MMA in CO_2 conducted in the presence of added stabilizer started homogeneously and became progressively more cloudy with increasing polymer formation and formed a kinetically stable colloidal dispersion. The successful formation of a stable colloid is a result of the interfacial activity of poly(FOA) in supercritical CO_2, which is indicative of a steric stabilization mechanism analogous to that obtained in conventional heterogeneous polymerizations that utilize nonionic surfactants (*4*, *24*). In all cases, the use of either LMW or HMW poly(FOA) as a stabilizer dramatically increased the yield and the molar masses of the product, in contrast to the results in polymerizations in which no polymeric stabilizer was added (see Table 1). The resulting product was easily isolated as a free-flowing powder after venting of the CO_2, which is an advantage of conducting such dispersion polymerizations in CO_2. Furthermore, residual monomer and stabilizer could be conveniently extracted from the resulting polymer in situ with a supercritical fluid extraction process to yield a highly purified product (*25*).

We did not observe major differences in the use of F-AIBN versus AIBN. Both initiators resulted in the formation of high molar mass polymer with high conversions when stabilizer was added. Uniform dispersions of polymer particles of high molar mass and high yields were obtained with both initiators as long as enough stabilizing agent was added, which is similar to results observed for conventional dispersion polymerizations (*8*, *26*, *27*). The primary particles have sizes ranging from 0.9 to 2.7 μm (Table 1), which is also consistent with the size of particles obtained with the use of classical dispersion polymerization processes (*2*).

We varied the concentration and molar mass of the polymeric stabilizer to investigate the influence of each factor on the stability of the colloid. For polymerizations in which F-AIBN and HMW poly(FOA) were used as the polymeric stabilizer, smaller and more uniform particles were formed as the concentration of added stabilizer was increased (Fig. 4). With progressive increases in the stabilizer concentration, the particles become more uniform and decreased in diameter as a result of successful colloidal stabilization. The molar mass of the polymeric stabilizer (at constant stabilizer concentration) also influenced the average size of the particles formed (Table 1). For both initiators, dispersion polymerizations using the LMW poly(FOA) resulted in stabilization of more particles with a smaller diameter than for polymerizations using the HMW poly(FOA) stabilizer (see Fig. 5). Moreover, because of the narrow size distribution of particles that could be obtained for certain reaction conditions (see Figs. 4C and 5A), especially for polymerizations that had a sufficient amount of HMW poly(FOA) to form a stable colloid, it is proposed that a fixed number of particles was reached early in the reaction for a given amount of stabilizer and that these particles grew at a relatively uniform rate. This situation is consistent with the initially homogeneous nature of the polymerizations.

In conclusion, poly(FOA) has been shown to be interfacially active in supercritical CO_2 and can effectively stabilize a dispersion polymerization. The successful formation of a stable colloid in supercritical CO_2 results in higher rates of polymerization and higher molar masses than without added stabilizer. Supercritical CO_2 offers an attractive alternative to conventional dispersing media for the synthesis of polymeric materials. This approach could eliminate the aqueous and organic waste streams typically generated from these manufacturing processes. In addition to these environmental advantages, the compressibility of the supercritical continuous phase should allow for the manipulation of the polymer morphology, affecting both the particle size and the particle size distribution. The creation of new core shell structures, interpenetrating polymer networks, or new composite materials that may not be readily accessible with conventional dispersing media may also be possible. With the successful stabilization of a polymer colloid in a low-viscosity, environmentally responsible supercritical fluid, it is now possible to consider the extension of this breakthrough into coating applications, an important technology that continues to come under significant environmental scrutiny, where there would be zero emission of hazardous volatile organic compounds to the atmosphere (*28*).

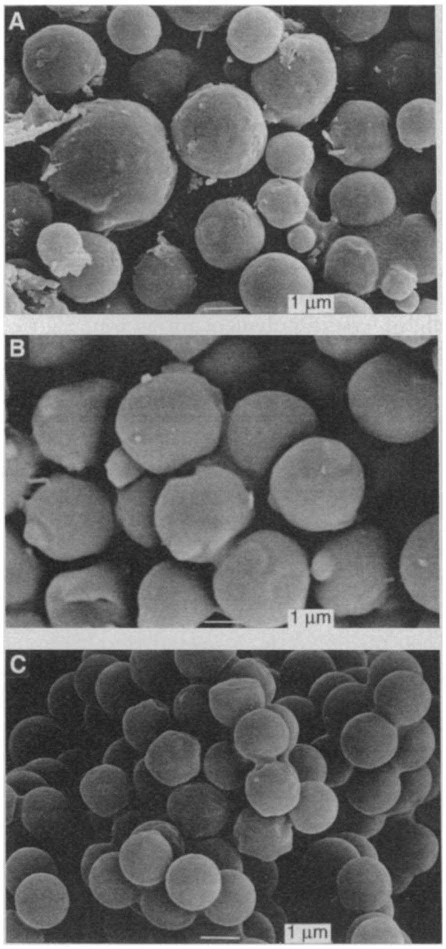


Fig. 4. Scanning electron micrographs of PMMA particles synthesized in CO_2 with F-AIBN used as the initiator and HMW poly(FOA) used as the stabilizer. (**A**) 1% (w/v) HMW poly(FOA); (**B**) 2% (w/v) HMW poly(FOA); (**C**) 4% (w/v) HMW poly(FOA).

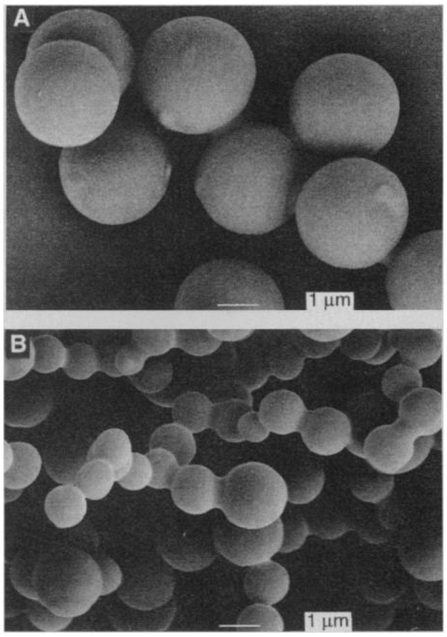


Fig. 5. Scanning electron micrographs of PMMA particles synthesized in CO_2 with AIBN used as the initiator and with (**A**) 2% (w/v) HMW poly(FOA) or (**B**) 2% (w/v) LMW poly(FOA).

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20. We have also reported on the synthesis and solubility characteristics of graft copolymers that have a fluorocarbon backbone [based on poly(1,1-dihydroperfluorooctyl acrylate)] either with hydrophilic grafts [based on poly(ethylene oxide)] or with hydrocarbon grafts (based on polystyrene) that have the appropriate solubility characteristics to also be effective surfactants for CO_2; see E. E. Maury *et al.*, *Polym. Prepr. Am. Chem. Soc. Div. Polym. Chem.* **34**, 664 (1993). We have also designed high molar mass triblock copolymers that contain fluorocarbon and hydrocarbon segments for utilization as surfactants and viscosity modifiers for CO_2; see Z. Guan and J. M. DeSimone, *ibid.*, p. 614.
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22. Percent conversions were determined gravimetrically. We determined molar masses by gel permeation chromatography (GPC) on a Waters 150-CV gel permeation chromatograph with Ultrastyragel columns of 100, 500, 10^3, and 10^4 Å porosities, using a tetrahydrofuran mobile phase and polystyrene standards (Showa Denko). We measured the average particle size by SEM.
23. Molar masses were determined at 3M by GPC on a Waters 410 DRI with a Jordi Associates Mixed Bed column packed in Freon-113 with a Freon-113 mobile phase.
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28. Union Carbide Chemicals & Plastics has developed a coating technology that replaces up to 80% of the solvents normally used in spray-coating formulations with CO_2. We believe that with the use of surfactants, coating processes could be developed with 100% of the solvents replaced by CO_2 for certain applications (perhaps in conjunction with a coalescing agent).

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Catalytic Activation of Carbon–Fluorine Bonds by a Soluble Transition Metal Complex

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Homogeneous catalytic activation of the strong carbon–fluorine bonds under mild conditions was achieved with the use of rhodium complexes as catalysts. The catalytic reactions between polyfluorobenzenes and hydrosilanes result in substitution of fluorine atoms by hydrogen atoms and are chemo- and regioselective. With individual stoichiometric steps observed and combined, and with intermediates isolated and fully characterized (including crystal structures), these systems demonstrate the effectiveness of a rational approach to catalytic design.

Homogeneous catalysis by transition metal complexes has an important role in chemistry, enabling efficient, selective processes under mild, easily controllable conditions and leading to the production of millions of tons of chemicals annually (*1*). These processes are based on the activation of chemical bonds by transition metals, followed by transformations in the metal coordination sphere and product release. Despite the phenomenal growth of this field, homogeneous catalysis by a metal complex based on activation of the strongest bond that carbon can form, C–F, remains unknown. Such catalysis is highly desirable for the functionalization of polyfluorinated organic compounds, which are important constituents of the chemical, pharmaceutical, and advanced materials industries (*2*). Toward this goal, much research effort has been devoted to the activation of the strong C–F bond by transition metal complexes. Indeed, C–F bond cleavage, although still fairly uncommon, is now known in a number of intermolecular systems involving transition metal complexes (*3–5*). However, despite this remarkable progress, all of these reactions are stoichiometric. We report here that aromatic C–F bonds can be cleaved by rhodium complexes even at room temperature and that this reaction can be elaborated into homogeneous catalysis involving C–F bonds. These catalytic cycles, which were designed by a combination of individual stoichiometric reactions, exhibit high selectivity.

The Rh(I) silyl complex $L_3RhSiMe_2Ph$ (**1a**) (L = PMe_3), synthesized from L_4RhCl and $LiSiMe_2Ph$ and structurally characterized (*6*, *7*), reacts quantitatively with C_6F_6 at room temperature:

$$\underset{\textbf{1a},\ R_3 = Me_2Ph \quad \textbf{1b},\ R_3 = Ph_3}{L_3RhSiR_3} + C_6F_6 \rightarrow \underset{\textbf{2}}{L_3RhC_6F_5} + R_3SiF \qquad (1)$$

The Me_2PhSiF product was identified unambiguously by ^{19}F and ^{1}H nuclear magnetic resonance (NMR) and by gas chromatography–mass spectroscopy (*8*). Complex **2** was characterized spectroscopically (*7*), and its identity was confirmed by an x-ray crystallographic study (*7*) (Fig. 1) and by its independent synthesis from L_4RhCl and C_6F_5MgBr. Interestingly, the

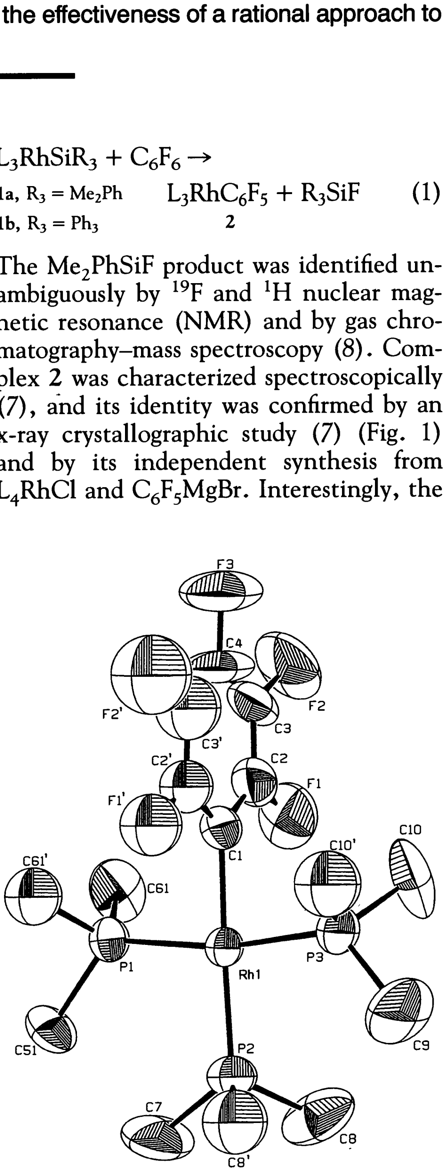

Fig. 1. Perspective view (ORTEP) of **2** (hydrogen atoms are omitted for clarity). Bond distances and angles (errors in last digits in parentheses) are Rh1-P1 = 2.292(2) Å; Rh1-P2 = 2.258(3) Å; Rh1-P3 = 2.291(2) Å; Rh1-C1 = 2.078(8) Å; P1-Rh1-P3 = 169.4(1)°; and P2-Rh1-C1 = 177.8(2)°.

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