Construction of Several Functionally-Substituted Tetramethylcyclopentadienyl Ligands, Their Use in the Syntheses of Several Organometallic Compounds, and Incorporation of the Organometallic Compounds into Polymers

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The syntheses of several functionally-substituted tetramethylcyclopentadienyl (FS-Cp*) ligands are reported. These ligands are significant because they possess functional groups that may be used in polymer construction. Several of the FS-Cp* ligands were used in the syntheses of organometallic monomers and clusters, which were then used in the construction of organometallic polymers.

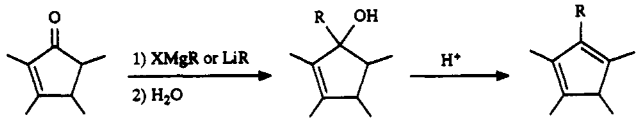
Introduction

The first use of a functionally-substituted cyclopentadienyl (FS-Cp) containing compound in the synthesis of an organometallic polymer was reported in 1955 by Arimoto and Haven.[2] Since that time, there have been several dozen additional reports which describe polymerizations of FS-Cp-containing organometallics.[3] In contrast, organometallic polymers which contain functionally substituted *permethylcyclopentadienyl* groups (FS-Cp*) have not been described.[4] Since organometallic compounds which contain the *permethyl*cyclopentadienyl (Cp*) ligand often exhibit significantly different properties than their cyclopentadienyl (Cp) analogues,[5] we endeavored to synthesize new FS-Cp*-containing organometallic compounds. In this paper, we describe the syntheses of several new FS-Cp* analogues of $Cp^*Mo(CO)_2(NO)$ and $Cp^*_3Mo_3(\mu_3\text{-}N)(O)(CO)_4$. In addition, we present a preliminary account of the use of these new FS-Cp*-containing organometallic compounds in the construction of organometallic polymers.

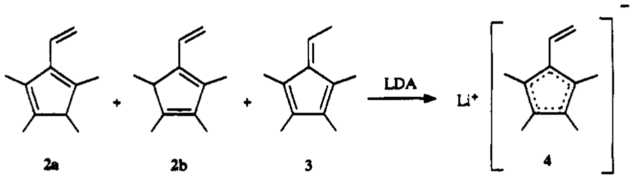
Results and Discussion

Construction of Two FS-Cp* Ligands and Their Use in the Syntheses of Several Organometallic Monomers. When ferrocene was first characterized in 1952, much attention was generated by the observation that the cyclopentadienyl (Cp) rings could be substituted via Friedel–Crafts type reactions.[6] This afforded a route to functionally-substituted ferrocenes which were appropriate for use in the construction of organometallic polymers. For example, vinylferrocene was synthesized by a route that involved Friedel–Crafts acylation of ferrocene.[2] However, syntheses that rely on Friedel–Crafts reactions of metal-coordinated Cp ligands are quite limited in scope because few organometallic compounds will tolerate the necessary reaction conditions.[7]

Scheme I



Scheme II



A more promising approach involves the substitution of cyclopentadiene prior to the synthesis of the desired FS-Cp-containing organometallic compound. To date, a number of new compounds have been prepared by this general strategy.[7] The strategy that we have adopted for the syntheses of FS-Cp*-containing organometallics is conceptually similar in that it also entails creation of functionally-substituted ligands prior to the syntheses of the desired organometallics. In order to synthesize the appropriate FS-Cp* ligands, we utilized a strategy which consists of reaction of an appropriate organolithium or Grignard reagent with 2,3,4,5-tetramethylcyclopent-2-enone (1), followed by dehydration of the resulting alcohol (Scheme I). We note that this strategy has been used previously, most notably in the very popular Burger/Jutzi–Kohl preparation of pentamethylcyclopentadiene.[8] In addition, several FS-Cp* ligands have recently been synthesized by this route by Okuda and co-workers[9] and

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(2) Aritmoto, F. S.; Haven, J. C., Jr. *J. Am. Chem. Soc.* **1955**, *77*, 6295.

(3) See, for example: (a) *Organometallic Polymers*; C. E. Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Academic Press: New York, 1978. (b) *Advances in Organometallic and Inorganic Polymer Science*; Carraher, C. E., Jr., Sheats, J. E., Pittman, C. U., Jr., Eds.; Marcel Dekker: New York, 1982. (c) Carraher, C. E., Jr. *J. Chem. Educ.* **1981**, *58*, 921. (d) Pittman, C. U., Jr.; Carraher, C. E., Jr.; Reynolds, J. R. In *Encyclopedia of Polymer Science and Technology*; John Wiley & Sons: New York, 1987; Vol. 10.

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(5) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*: University Science Books: Mill Valley, CA, 1987.

(6) Woodward, R. B.; Rosenblum, M.; Whiting, M. C. *J. Am. Chem. Soc.* **1952**, *74*, 3458.

(7) See, for example: Macomber, D. W.; Hart, W. P.; Rausch, M. D. *Adv. Organomet. Chem.* **1982**, *21*, 1 and references cited therein.

(8) (a) Burger, U.; Delay, A.; Mazenod, F. *Helv. Chim. Acta* **1974**, *57*, 2106. (b) Kohl, F. X.; Jutzi, P., *J. Organomet. Chem.* **1983**, *243*, 119.

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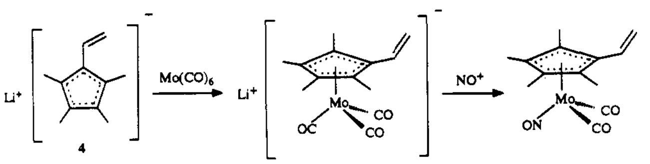
Scheme III



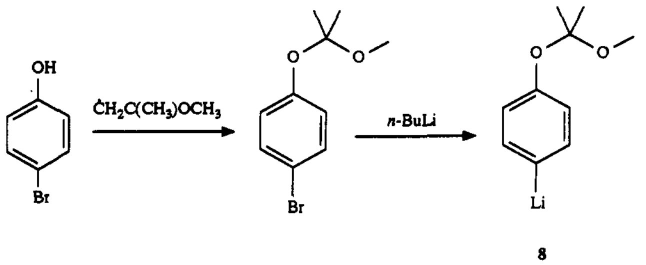
by Mintz and co-workers.[10]

In a recent paper, Mintz and co-workers reported that the reaction of vinylmagnesium bromide with 1 gives, after hydrolysis and subsequent acid-catalyzed dehydration, the tautomeric products 1-vinyl-2,3,4,5-tetramethylcyclopentadiene (two isomers, **2a** and **2b**), and 2,3,4,5,6-pentamethylfulvene (**3**).[10b] Mintz demonstrated that anionic nucleophiles add to **3**, and he has exploited this reaction to create several bifunctional FS-Cp* ligands which appear to be appropriate for use in the syntheses of heterobimetallic compounds. We reasoned, on the basis of previous work with 6-methylfulvene,[7] that the reaction of **3** with the sterically hindered base lithium diisopropylamide (LDA) would result in the deprotonation of **3**, with concomitant isomerization of the charge into the ring. In fact, LDA cleanly converts the inseparable mixture of **2** and **3** into Li[C_5Me_4—CH=CH_2] (**4**; Scheme II).[11] In most instances, we synthesized **4** from a mixture of **2** and **3** and then reacted **4** in situ to create the desired organometallic compounds. Compound **4** may, however, be isolated as a dry gray powder which is stable under an atmosphere of dry nitrogen. Typical isolated yields of **4** were ca. 60%.

Our initial attempts to use **4** in the synthesis of a FS-Cp*-containing organometallic compound focused on the synthesis of (η^5-C_5Me_4—CH=CH_2)Mo$(CO)_2$NO (**5**). One of the reasons that we selected **5** as our initial target molecule was that the analogous FS-Cp-containing molecule had been synthesized and used in the creation of organometallic polymers.[12] Consequently, there was some precedent to guide us in our later syntheses of polymers. Another reason was that the analogous Cp* containing compound is suitable for use in the synthesis of an unusual nitride-containing cluster.[13] Thus by first synthesizing **5**, we would then have the opportunity to use **5** in the synthesis of a cluster which could then be used in the synthesis of a cluster-containing polymer.

Our synthesis of **5** was based on the syntheses of the analogous CpMo$(CO)_2$NO and Cp*Mo$(CO)_2$NO.[14,15] As illustrated in Scheme III, reaction of **4** with Mo$(CO)_6$ resulted in the synthesis of Li[(η^5-C_5Me_4—CH=CH_2)Mo$(CO)_3$], which was treated in situ with a solution of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald, a convenient source of NO⁺). After appropriate workup of the resulting materials (including purification by column chromatography), **5** was isolated as a slightly tacky orange solid. The yield of the product, 37% (95% pure, vide infra), compares quite favorably to the 41% yield reported for the analogous Cp*Mo$(CO)_2$NO.[15]

Scheme IV



NMR analysis of the product revealed that small amounts ($\leq$5%) of organic impurities were present. This conclusion was consistent with the elemental analysis which revealed slightly high carbon, high hydrogen, and low nitrogen content. Our conclusion was that the product was contaminated with ca. 5 mol % of a mixture of unreacted **2** and **3** or with some oligomeric material derived from **2** and **3**. While we have found that this impure material can be used in the synthesis of organometallic polymers (and clusters), the syntheses reported herein were conducted with a material that was freed from the organic impurities by three successive sublimations (39 °C, 10^{-4} Torr). After each sublimation, a small amount of orange oil remained in the bottom of the sublimer. The amount remaining, however, was less after each sublimation. The NMR spectrum of the oil was quite complex, which suggested the presence of oligomeric material. No further attempt was made to characterize this oil. After these sublimations, a purer material was obtained, but the final isolated yield was reduced to about 20%. The purified material gave clean NMR spectra and satisfactory elemental analysis.

Compound **5**, which contains a vinyl-substituted permethylcyclopentadienyl ligand, is suitable for use in the creation of organometallic polymers via *chain* reactions (vide infra). We were also anxious to synthesize FS-Cp*-containing organometallic compounds that could be incorporated into polymeric supports via condensation reactions. To this end, we decided to synthesize Na[C_5Me_4-*p*-C_6H_4OR] (**6**, R = CMe_2OMe), which possesses a protected *p*-hydroxyphenyl substituent. In order to synthesize **6** via the general route outlined in Scheme I, it was first necessary to synthesize an appropriate organolithium reagent. We began by masking the rather acidic phenolic proton of *p*-bromophenol by reaction with 2-methoxypropene (**7**). Treatment with *n*-butyllithium resulted in transmetalation to give the desired organolithium reagent *p*-LiC_6H_4OR (**8**, R = CMe_2OMe) as a dry white powder (Scheme IV). An assay of **8** by a modified Gilman double titration[16,17] indicated that the powder contained 0.5 mol of hexane/mol of **8**.

Treatment of a solution of **1** with a solution of **8** followed by dehydration of the resulting alcohol (Scheme I, MR = *p*-Li$C_6H_4C(Me)_2OMe$) afforded 1-(*p*-hydroxyphenyl)-2,3,4,5-tetramethylcyclopentadiene (**9**). Since the proposed synthesis of the desired (η^5-C_5Me_4-*p*-C_6H_4OR)Mo$(CO)_2$NO

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[9] Okuda, J.; Zimmerman, K. H. *J. Organomet. Chem.* **1988**, *344*, C1.

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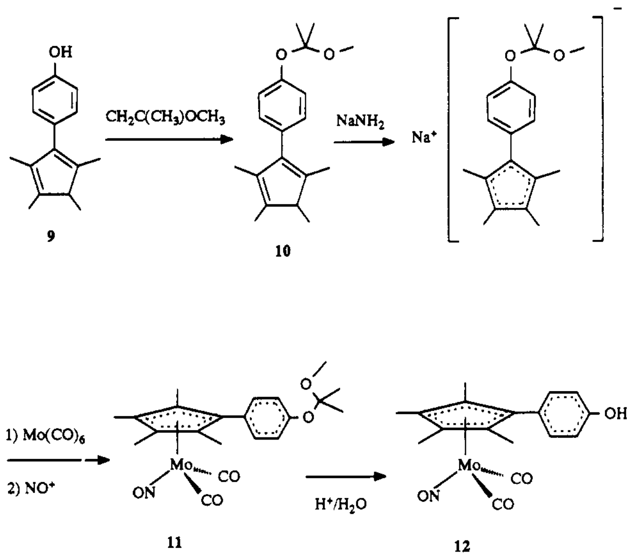
Scheme V



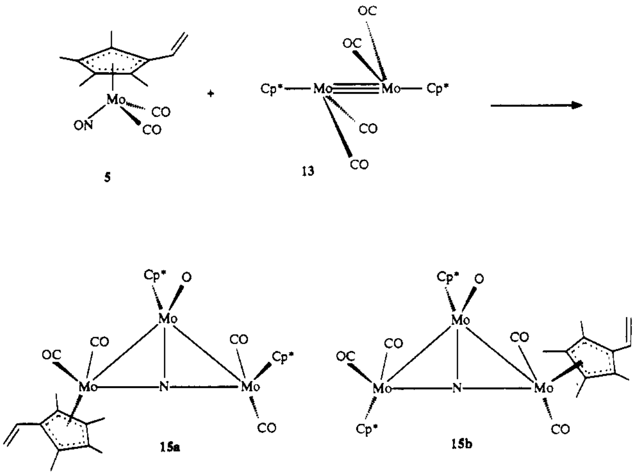
complex required treatment of $Mo(CO)_6$ with a ring-deprotonated (anionic) version of **9**, it was necessary to mask the phenolic proton of **9** by reaction with **7**. As illustrated in Scheme V, the resulting product, HC_5Me_5–(p-C_6H_5OR) (**10**, R = CMe_2OMe), was then deprotonated via reaction with sodium amide and subsequently treated with $Mo(CO)_6$, followed by Diazald, to give (η^5-C_5Me_4-p-C_6H_4OR)-$Mo(CO)_2NO$ (**11**, R = CMe_2OMe). The protecting group was removed from **11** to give the desired p-hydroxyphenyl-containing (η^5-C_5Me_4-p-C_6H_5OH)$Mo(CO)_2NO$ (**12**), which was recrystallized from hexane/ethanol. The ^1H NMR spectrum of the product indicated that the resulting microcrystalline powder contained 0.5 mol of ethanol of crystallization/mol of **12**.

Syntheses of Several Organometallic Clusters Which Contain Functionally-Substituted Tetramethylcyclopentadienyl Ligands. In 1985, we reported that the photolytic reaction of $Cp^*Mo(CO)_2NO$ with $Cp^*_2Mo_2(CO)_4$ (**13**) afforded the new trimolybdenum cluster $Cp^*_3Mo_3(\mu_3\text{-}N)(O)(CO)_4$ (**14**), which contained a cluster-coordinated nitride ligand.[13] Since we were interested in creating polymers which contain discrete organometallic clusters and since we had synthesized several functionally-substituted analogues of $Cp^*Mo(CO)_2NO$ (viz. **5**, **11**, and **12**), we decided to attempt to synthesize several new functionally-substituted analogues of **14**.

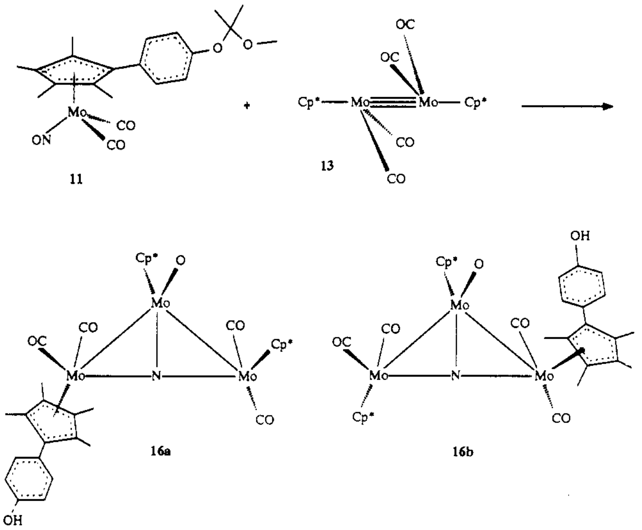
The first of the functionally-substituted clusters that we attempted to synthesize was (η^5-C_5Me_4—CH=CH_2)-$(Cp^*)_2Mo_3(\mu_3\text{-}N)(O)(CO)_4$ (**15**). Photolysis of a solution of **5** and **13**, followed by separation of the products via column chromatography, afforded **15** as a green microcrystalline powder (Scheme VI). The infrared spectrum of **15** confirmed its characterization as the analogue of **14** since the CO stretching region of the two infrared spectra were virtually indistinguishable. In addition, both **15** and **14** exhibit a strong absorbance at 630 nm (ϵ = 4390 M^{-1} cm^{-1} for **15**, 4300 M^{-1} cm^{-1} for **14**). Recrystallization of the product from $CHCl_3$ gave **15**·$CHCl_3$. In the prototype cluster **14**, the Mo_3 cluster core contains two different "basal" Mo atoms, and an "apical" Mo atom. ^1H and ^{13}C NMR spectra of **15** revealed that the product consisted of two isomeric forms in which the unique FS-Cp* ligand was coordinated to one or the other of the two "basal" Mo atoms.

The synthesis of the analogous p-hydroxyphenyl cluster (η^5-C_5Me_5-p-C_6H_4OH)$(Cp^*)_2Mo_3(\mu_3\text{-}N)(O)(CO)_4$ (**16**) was accomplished via the photolysis of a solution which contained **13** and the protected hydroxyphenyl monomer **11**, followed by separation of the products via column chromatography (Scheme VII). While the desired cluster **16** was isolated as the major product (22%), a small amount of the protected hydroxyphenyl analogue (η^5-C_5Me_4-p-C_6H_4OR)$(Cp^*)_2Mo_3(\mu_3\text{-}N)(O)(CO)_4$ (**17**, R = CMe_2OMe) was also recovered. Attempts to synthesize **16** from **13** and the unprotected monomer **12** were unsuccessful. Recrystallization of **16** from toluene/hexane gave a dry crystalline powder which contained 1 mol of hexane of crystallization/mol of **16** (**16**·hex).

Scheme VI



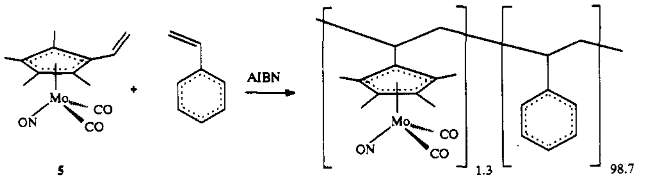
Scheme VII



Characterization of **16**·hex via infrared spectroscopy indicated that the FS-Cp*-containing analogue of **14** had been synthesized since the carbonyl stretching regions of the spectra of **14** and **16**·hex were virtually indistinguishable. In addition, a distinct peak at 3580 cm^{-1}, which was assigned to the O–H stretch of phenol, was observed in the infrared spectrum of **16**. The UV/visible spectrum of **16** was similar to the spectrum of **14**, with an intense band (ϵ = 4460 M^{-1} cm^{-1}) observed at 630 nm. Characterization of **16** by ^1H NMR spectroscopy revealed the presence of two isomeric forms which differed in that the FS-Cp* was bound to one or the other of the basal Mo atoms.

Incorporation of the Vinyl-Substituted Compounds 5 and 15 into Polymeric Supports. The ultimate goal of this program was to synthesize polymers in which metal-containing moieties were coordinated to FS-Cp* ligands, which were in turn covalently bound to the

Scheme VIII



polymer backbone. Presumably, such polymers would be less susceptible to "metal leaching" than are polymers which rely on relatively weak dative bonds to secure the metal to the support.[18]

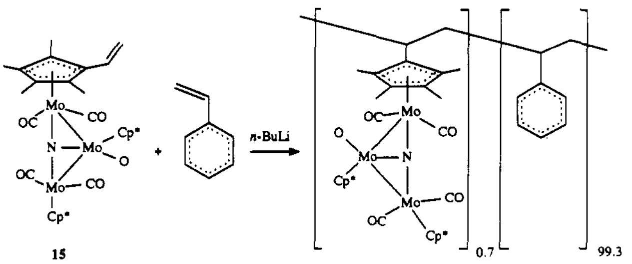
Our attempts to homopolymerize **5** included reactions in the presence of a free radical initiator (AIBN), an anionic initiator (*n*-butyllithium), and by exposure to UV radiation. All such attempts failed to produce any isolable polymer. In fact, the failures of these attempted polymerizations were expected due to the steric bulk about the vinyl substituent. For steric reasons, the vinyl substituent of **5** is almost certainly required to adopt the exo configuration. In this orientation, reaction of the α-carbon of the vinyl substituent would be severely inhibited because of the nearby methyl substituents of the FS-Cp* ligand. Thus attack of the initiator at the accessible β-carbon of the vinyl substituent may be relatively facile, but participation of the sterically-encumbered α-carbon is undoubtedly sluggish. In view of the failure of **5** to homopolymerize, we made no attempt to homopolymerize the larger vinyl-substituted cluster **15**.

While homopolymerization of **5** (and presumably **15**) was not possible for steric reasons, we reasoned that copolymerization with a much smaller (and more reactive) organic substrate might be possible, especially if the organic substrate were present in excess. We selected styrene as the organic comonomer and attempted to form a copolymer from solutions which contained styrene and **5** in a molar ratio of 95.2 to 4.8. Attempted polymerizations with *n*-butyllithium added as an initiator failed, possibly due to attack of the initiator at the nitrosyl or carbonyl ligands rather than at the vinyl substituents of the monomers. However, attempted polymerizations with added AIBN (1 mol %) were successful (Scheme VIII).

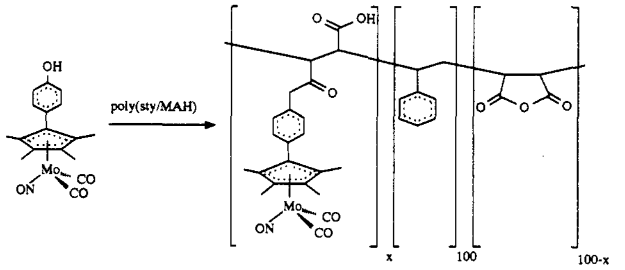
Once the desired styrene–**5** copolymer had been isolated and purified, it was characterized via solution ^{1}H NMR spectroscopy, infrared spectroscopy, and several other techniques. The solution NMR spectrum of the copolymer closely resembled the NMR spectrum of atactic polystyrene.[19] The broad resonance near δ 1.5 was assigned to the secondary protons of the polymer backbone, while the broad resonance near δ 1.9 was assigned to the tertiary protons of the polymer backbone and methyl protons of **5**. In addition, broad resonances due to the aromatic protons were observed in the vicinity of δ 6.3–6.5. Perhaps the most significant feature of the NMR spectrum was the complete lack of any resonance which could be due to the olefin protons of unreacted **5**. The failure to detect olefin protons is consistent with the conclusion that **5** is chemically incorporated into the polymer and mitigates against the possibility that the polymer is a simple mixture of polystyrene and **5**.

Determination of the amount of **5** that had been incorporated into the polymer was accomplished by a Beer's law analysis using the infrared spectrum of the product.

Scheme IX



Scheme X



We first determined the extinction coefficients of the 1602-cm^{-1} absorbance of an authentic sample of polystyrene and the 2001- and 1922-cm^{-1} absorbances of **5**. By comparing the intensities of the appropriate absorbances of the copolymer, we determined that it contained 98.7 mol % styrene to 1.3 mol % **5**.

The average molecular weight of the copolymer was determined to be 21 000 via the solution viscosity method at 25 °C, using (nearly) monodisperse polystyrene samples of known molecular weight as calibration standards, and toluene as the sovlent.[20,21] In view of the average molecular weight of the polymer and the content of the organometallic moiety, we can conclude that the "average" polymer chain contains one organometallic fragment. Perhaps reaction of the growing polymer chain with the organometallic moiety represents a chain termination step.

Our experience with the monomer **5** led us to believe that the vinyl-substituted cluster **15** could also be copolymerized with styrene. However, attempts to copolymerize styrene with **15** in the presence of AIBN failed. A successful copolymerization of styrene and **15** (in a ratio of 99.0 mol % styrene to 1.0 mol % **15**) was accomplished via use of the anionic initiator *n*-butyllithium (Scheme IX). After purification, the resulting polymer was assayed via infrared spectroscopy in order to determine its composition. Beer's law analysis using the large 1880-cm^{-1} absorbance of **15** (ϵ = 5.08 L g^{-1} cm^{-1}), and the 1602-cm^{-1} peak of polystyrene revealed that the polymer contained 0.70 mol % **15**. No attempt was made to further characterize the polymer.

Incorporation of the *p*-Hydroxyphenyl-Substituted Compounds 12 and 16 into Polymeric Supports. Our rationale for synthesizing the *p*-hydroxyphenyl-substituted FS-Cp* ligand was that organometallic compounds with this ligand could be incorporated into polymeric supports via condensation reactions. In most common condensation polymerizations, monomers are used which contain two functional groups capable of participating in condensation reactions. Since **12** and **16** each contain only one such group, polymerizations of this type are not possible. We reasoned, however, that these compounds could be in-

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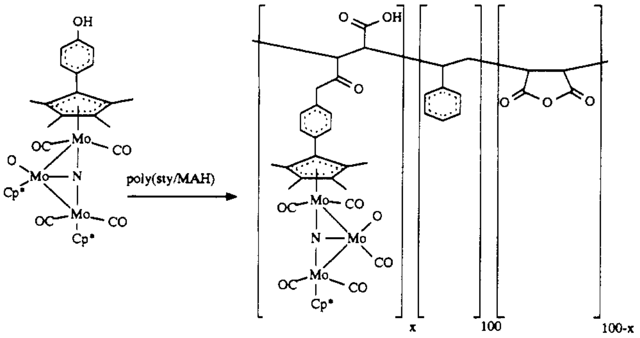
Scheme XI



corporated into polymeric supports by reaction with preformed polymers that contain functional groups capable of coupling with phenol. In these preliminary studies, we reacted compounds **12** and **16** with a preformed 1/1 copolymer of styrene and maleic anhydride (poly(sty–mah); M_n = 1600), in the presence of 4-(dimethylamino)pyridine. In the reaction of **12**·$^1/_2$EtOH with poly(sty–mah), the reagents were added in such a way that the initial ratio of maleic anhydride moieties to **12** was 95.2 mol % mah to 4.8 mol % **12** (Scheme X). The resulting orange polymeric product was isolated, purified, and then analyzed by infrared spectroscopy. A Beer's law analysis, utilizing the 2002- and 1925-cm^{-1} absorbances of the organometallic and the 1603-cm^{-1} absorbance of poly(sty–mah) revealed that 2.8 mol % **12** had been incorporated into the polymer.

The reaction of poly(sty–mah) with **16**·hex was run with a ratio of 99.1 mol % mah to 0.90 mol % **16** (Scheme XI). The resulting dark green polymeric product was isolated and purified by conventional methods. The use of infrared spectroscopy to determine the amount of **16** that had been incorporated into the polymer was not feasible because absorbances due to poly(sty–mah) overlap with the strong 1880-cm^{-1} absorbance of **16**. However, since the cluster has an intense absorbance at 630 nm, we were able to use visible spectroscopy to determine that 0.64 mol % **16** had been incorporated into the polymer.

Conclusion

In this paper, we have described a general strategy by which new FS-Cp* ligands may be made. In particular, we have described the syntheses of the vinyl-substituted ligand **4**, and the (protected) *p*-hydroxyphenyl-substituted ligand **6**. The vinyl-substituted ligand **4** was used in the syntheses of organometallic compounds **5** and **15**, which were copolymerized with styrene. Since the steric bulk close to the vinyl substituents of **5** and **15** apparently led to relatively low reactivity, future studies of similar compounds will focus on compounds in which the ring substituent is a rather long ω-alkenyl group. We have also shown that organometallic compounds with the *p*-hydroxyphenyl-substituted FS-Cp* will participate in useful coupling reactions. Efforts to exploit this chemistry in order to create new organometallic polymers (including step-growth polymers) and heterobimetallics are in progress.[4,22]

Experimental Section

General Reaction Conditions and Reagents. All reactions were performed under an atmosphere of dry N_2 using conventional techniques.[23] Solvents were purified by distillation from appropriate drying agents under an atmosphere of dry N_2.[24] Solutions of *n*-butyllithium in hexanes were assayed prior to use via the double titration method.[16,17] AIBN was recrystallized from ethanol prior to use. Styrene was freshly distilled immediately prior to use. Hydrated $CeCl_3$ was dehydrated by reaction with $SOCl_2$. 1,2,3,4-Tetramethylcyclopent-2-enone (**1**),[8] $Cp^*_2Mo_2(CO)_4$ (**13**),[25] and mixtures of 1-vinyl-2,3,4,5-tetramethylcyclopentadiene (**2**) and 1,2,3,4,6-pentamethylfulvene (**3**)[10b] were prepared according to published procedures. All other reagents were obtained from major suppliers and used without further preparation.

Analyses. IR spectra were recorded using either a Perkin-Elmer 1310 spectrophotometer or a Mattson Cygnus-100 FT-IR spectrophotometer. UV/visible spectra were measured on a Hewlett-Packard 8452 diode array spectrophotometer. NMR spectra were recorded using a JEOL 270-GX spectrometer. ^{1}H and ^{13}C NMR spectra were collected in $CDCl_3$ and were referenced to TMS which was included as an internal standard. Mass spectra were measured with a Finnigan 4021 mass spectrometer at the WVU Department of Biochemistry.

Synthesis of (η^5-C_5Me_4—CH=CH_2)Mo(CO)$_2$NO (5). A 500-mL flask was charged with 100 mL of THF and 3.44 g (34.0 mmol) of diisopropylamine. After cooling the flask and its contents to 0 °C, 13.6 mL (34.0 mmol) of 2.50 M *n*-butyllithium was added. The solution was stirred at 0 °C for 1 h and then warmed to room temperature. To this solution of lithium diisopropylamide (LDA) was added 4.44 g (30.0 mmol) of the mixed isomers **2** and **3**. The solution was then stirred at room temperature overnight. The resulting solution of Li[C_5Me_4—CH=CH_2] (**4**) was then treated with 8.72 g (33.0 mmol) of $Mo(CO)_6$. The mixture was refluxed for 48 h, cooled to room temperature, and then slowly treated with a solution of 7.06 g (33.0 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (Diazald) in 50 mL of THF. After the resulting solution was allowed to stir for 1 h, solvent was removed in vacuo to give a red-brown residue. The residue was purified via column chromatography (neutral alumina, activity III), and the orange band that was eluted with hexane was collected. Evaporation of the solvent afforded **5** as a slightly tacky, orange solid. ^{1}H NMR spectra indicated that the material contained a small amount of impurities (≤5%). The yield of this impure material was 3.74 g (11.1 mmol of **5**, 37% yield assuming 95 mol % purity). Analytically pure **5** (2.00 g, 6.08 mmol, 20.3% yield) was obtained following three successive sublimations of the impure product at 37 °C, 10^{-4} Torr.

Analytical Data for 5. ^{1}H NMR: δ 2.05 (6 H, s, CH_3), 2.13 (6 H, s, CH_3), 5.22 (1 H, dd, $^3J_{cis}$ = 11.4 Hz, $^2J_{gem}$ = 1.3 Hz, endo CH=C*H*H), 5.34 (1 H, dd, $^3J_{trans}$ = 17.8 Hz, $^2J_{gem}$ = 1.3 Hz, exo CH=CH*H*), 6.44 (1 H, dd, $^3J_{cis}$ = 11.4 Hz, $^3J_{trans}$ = 17.9 Hz, C*H*=CH_2). ^{13}C NMR: δ 10.6 (CH_3), 11.6 (CH_3), 105.6 (ring *C*), 106.9 (ring *C*), 107.0 (ring *C*), 116.5 (CH=*C*H_2), 128.4 (*C*H=CH_2), 229.6 (*C*O). Unequivocal ^{13}C NMR spectral assignments were based on a separate off-resonance decoupled spectrum. IR (CH_2Cl_2): ν_{CO} 2006 (vs, ε = 6.78 L g^{-1} cm^{-1}), 1928 cm^{-1} (vs, ε = 7.86 L g^{-1} cm^{-1}); ν_{NO} 1649 cm^{-1} (vs). UV/visible (hexane): λ_{max} 480 (ε = 139 M^{-1} cm^{-1}), 370 nm (ε = 667 M^{-1} cm^{-1}). Mass spectrum (electron impact): the envelope which corresponded to the parent ion fell between *m/e* 333 and 325 and exhibited the predicted shape. Melting point: 59.0–59.5 °C. Elemental analysis (Oneida): 47.7% C, 4.8% H, and 4.3% N observed; 47.4% C, 4.6% H, and 4.3% N expected.

Preparation of *p*-BrC_6H_4—OCMe$_2$OMe. A 250-mL flask was covered with aluminum foil in order to protect the contents from the light. The flask was then charged with 19.2 mL (200 mmol) of 2-methoxypropene (**7**) and 17.3 g (100 mol) of *p*-bromophenol. A drop of phosphorus oxychloride was added, and the mixture was allowed to stir at room temperature for 1 h. The reaction was then quenched with five drops of triethylamine.

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Evaporation of the solvent in vacuo afforded 24.9 g (98 mmol, 98% yield) of *p*-BrC_6H_4–$OCMe_2OMe$ as a light-sensitive colorless oil.

Analytical Data for *p*-BrC_6H_4—$OCMe_2OMe$. ^1H NMR: δ 1.44 (6 H, s, CH_3), 3.37 (3 H, s, CH_3), 6.97 (2 H, d, ^3J = 8.7 Hz, ring *H* ortho to OR), 7.34 (2 H, d, ^3J = 8.7 Hz, ring *H* meta to OR).

Preparation of *p*-LiC_6H_4—$OCMe_2OMe\cdot{}^1/_2C_6H_{14}$ (8·$^1/_2C_6H_{14}$). A flask was covered with aluminum foil and then charged with 24.9 g (97.9 mmol) of *p*-BrC_6H_4-$OCMe_2OMe$ and 150 mL of hexane. A 40.8-mL aliquot of 2.34 M *n*-butyllithium (110 mmol) was added, and the mixture was stirred for 4 h, during which time a white precipitate formed. The solution was then filtered. The resulting white precipitate was washed with hexane and then dried in vacuo. Analysis of the white solid indicated the presence of 0.5 mol of hexane of crystallization/mol of the lithium reagent.[17] The yield of product was 14.2 g (66.4 mmol, 67.7% yield). The product was white and pure when freshly made but turned pink when stored over a period of time. Accordingly, this compound was freshly made before each use.

Preparation of HC_5Me_4-*p*-C_6H_4OH (9). A 250-mL flask was charged with 17 g of $CeCl_3$ (69 mmol) and 50 mL of THF. The mixture was stirred, cooled to 0 °C, and then aged for 1 h.[26] To this suspension was added dropwise a mixture of 14.2 g (66 mmol) of 8·$^1/_2C_6H_{14}$ and 50 mL of THF. After stirring for 1 h at room temperature, the solution was cooled to 0 °C, and a solution of 8.25 g (60 mmol) of **2** and **3** in 50 mL of THF was added. The mixture was warmed to room temperature and then stirred overnight. The reaction was then quenched with 50 mL of 10% HCl (aqueous). The mixture was stirred for 3 h and then extracted with ether. The ether extracts were first washed with aqueous $NaHCO_3$ and then water and finally were dried over sodium sulfate. Removal of the ether in vacuo afforded 13.61 g (47.5 mmol, 79.6% yield) of **9** as an orange oil.

Analytical Data for 9. ^1H NMR: δ 0.93 (3 H, d, CH-CH_3), 1.84 (3 H, s, C-CH_3), 1.90 (3 H, s, C-CH_3), 1.98 (3 H, s, C-CH_3), 3.12 (1 H, q, *CH*-CH_3), 5.68 (1 H, br s, O*H*), 6.92 (2 H, d, phenyl *H*), 7.10 (2 H, d, phenyl *H*). IR (neat): ν_{OH} 3350 cm^{-1} (s, br).

Preparation of HC_5Me_4-*p*-$C_6H_4OCMe_2OMe$ (10). A 250-mL flask was covered with aluminum foil and then charged with 9.1 mL (95 mmol) of **7** and 13.6 g (47.5 mmol) of **9**. A drop of phosphorus oxychloride was added, and the mixture was allowed to stir at room temperature for 1 h. The reaction was then quenched with five drops of triethylamine. Evaporation of the solvent in vacuo afforded an orange oil which was purified via column chromatography on basic alumina. Elution of the column with 50% (v/v) ether/hexane afforded a yellow band which yielded, upon evaporation of the solvents in vacuo, 5.93 g (20.7 mmol, 43.6% yield) of **10** as a viscous orange oil.

Analytical Data for 10. ^1H NMR: δ 0.94 (3 H, d, CH-CH_3), 1.51 (6 H, s, C(CH_3)$_2$OMe), 1.86 (3 H, s, C-CH_3), 1.92 (3 H, s, C-CH_3), 2.04 (3 H, s, C-CH_3), 3.15 (1 H, q, *CH*-CH_3), 3.44 (3 H, s, CMe_2OCH_3), 7.10 (4 H, AB quartet, phenyl *H*).

Preparation of (η^5-C_5Me_4-*p*-$C_6H_4OCMe_2OMe$)Mo(CO)$_2$NO (11). A 150-mL flask was charged with 1.70 g (43.4 mmol) of $NaNH_2$ and 20 mL of THF. After the flask was cooled to 0 °C, a solution of 9.93 g (34.7 mmol) of **10** in 50 mL of THF was slowly added. The resulting suspension was stirred at 0 °C for 1 h and then at room temperature for an additional 24 h. The volume of the solution was reduced to 25 mL in vacuo, and the solution was filtered. The precipitate was washed with two 10-mL portions of THF, and the washings and filtrate, which contained Na[C_5Me_4-*p*-$C_6H_4OCMe_2OMe$], were combined and placed in a 500-mL flask. After the solution was diluted with 150 mL of THF, 9.77 g (37.0 mmol) of Mo(CO)$_6$ was added. The solution was refluxed for 16 h, cooled to room temperature, and then slowly treated with a solution of 7.93 g (37.0 mmol) of Diazald in 50 mL of THF. After the solution was allowed to stir for 1 h, the solvent was removed in vacuo to give a red-brown residue. The mixture was purified via column chromatography (neutral alumina, activity III); the orange band that eluted with hexane was collected. Evaporation of the solvent from this orange solution gave 5.26 g of **11** (11.3 mmol, 32.6% yield) as a dry orange powder.

Analytical Data for 11. ^1H NMR: δ 1.49 (6 H, s, OCH-(CH_3)$_2$OMe), 1.99 (6 H, s, C-CH_3), 2.08 (6 H, s, C-CH_3), 3.42 (3 H, s, $OCMe_2OCH_3$), 7.09 (4 H, AB quartet, phenyl *H*). ^{13}C NMR: δ 10.8 (C-CH_3), 11.3 (C-CH_3), 25.1 (OC(CH_3)$_2$OCMe), 49.1 ($OCMe_2OCH_3$), 103.6 (O*C*Me_2OMe), 105.6, 108.9, 113.1 (C_5 ring carbons), 120.6 (phenyl carbon, ortho to OR), 127.0 (phenyl carbon, para to OR), 132.4 (phenyl carbon, meta to OR), 154.5 (phenyl carbon, ipso to OR), 229.9 (*C*=O). IR (CH_2Cl_2): ν_{CO} 2005 (vs), 1927 cm^{-1} (vs); ν_{NO} 1647 cm^{-1} (vs). UV/visible (hexane): λ_{max} 484 (ϵ = 81 M^{-1} cm^{-1}), 370 nm (ϵ = 486 M^{-1} cm^{-1}). Melting point: 89.5–90.5 °C.

Preparation of (η^5-C_5Me_4-*p*-C_6H_4OH)Mo(CO)$_2$NO·$^1/_2$EtOH (12·$^1/_2$EtOH). A 100-mL flask was charged with 1.01 g (2.16 mmol) of **11** and 30 mL of ether. To this solution was added a solution of 0.10 g (0.53 mmol) of *p*-toluenesulfonic acid in 2.0 mL of deoxygenated water. The mixture was stirred for 3 h, after which time the aqueous layer was removed. The organic layer was extracted with deoxygenated water until the pH of the water washings was greater than 6, and then it was dried with sodium sulfate. Removal of the ether in vacuo gave a red oil. The red oil was triturated with anhydrous ethanol and then recrystallized from ethanol/hexane at −20 °C to give 0.66 g (1.66 mmol, 77% yield) of **12**·$^1/_2$EtOH.

Analytical Data for 12·$^1/_2$EtOH. ^1H NMR: δ 1.1 (t, CH_2CH_2OH), 1.97 (6 H, s, C—CH_3), 2.07 (6 H, s, C—CH_3), 3.6 (m, CH_3CH_2OH), 4.81 (1 H, br s, O*H*), 6.81 (2 H, d, phenyl *H* meta to OH, ^3J = 8.4 Hz), 7.08 (2 H, d, phenyl *H* ortho to OH, ^3J = 8.8 Hz). ^{13}C NMR: δ 10.7 (C—CH_3), 11.2 (C—CH_3), 17.2 (CH_3CH_2OH), 56.8 (CH_3CH_2OH), 105.6, 108.7, 113.2 (C_5 ring carbons), 115.1 (phenyl carbon ortho to OH), 124.5 (phenyl carbon para to OH), 132.8 (phenyl carbon meta to OH), 155.4 (*C*—OH), 22.90 (*C*=O). IR (CH_2Cl_2): ν_{OH} 3581 cm^{-1} (br, m); ν_{CO} 2005 (vs), 1927 cm^{-1} (vs); ν_{NO} 1646 cm^{-1} (vs). IR (THF): ν_{CO} 2001 (vs, ϵ = 5.56 L g^{-1} cm^{-1}), 1927 cm^{-1} (vs, ϵ = 7.61 L g^{-1} cm^{-1}); ν_{NO} 1646 cm^{-1} (vs). UV/visible (hexane): λ_{max} 478 (ϵ = 106 M^{-1} cm^{-1}), 370 nm (ϵ = 581 M^{-1} cm^{-1}). Mass spectrum (electron impact): the envelope which corresponds to the parent ion falls between *m/e* 391 and 399; the relative intensities of the observed peaks closely matched the predicted values. Melting point: 74.0 °C. Elemental analysis (Galbraith): 52.5% C, 4.6% H, and 3.3% N observed; 51.7% C, 4.8% H, and 3.3% N expected.

Preparation of (η^5-C_5Me_4—CH=CH_2)(Cp*)$_2$Mo$_3$(μ_3-N)(O)(CO)$_4$ (15). A water-cooled Pyrex immersion well photolysis reactor was charged with 0.331 g (1.01 mmol) of **5**, 1.15 g (2.00 mmol) of **13**, and 250 mL of toluene. The solution was irradiated for 1 h with a 450-W Hanovia medium-pressure mercury-vapor lamp. During this time, a steady stream of nitrogen was bubbled through the solution in order to facilitate removal of evolved carbon monoxide. The solvent was removed from the resulting red-brown solution in vacuo. To the red-brown residue was added some neutral activity III alumina (ca. 5 g) and some CH_2Cl_2. The solvent was removed in vacuo leaving a red-brown powder, which was then transferred onto the top of a chromatography column which had been packed in hexane. Elution of the column with toluene led to the collection of a broad orange-red band which contained **5**, **13**, and Cp*$_2$Mo$_2$(CO)$_6$. (These compounds were identified by their NMR and IR spectra).[25] Subsequent elution with 1% (v/v) THF/toluene resulted in the isolation of a green band which contained **15**. The solvents were removed in vacuo, yielding 0.231 g (0.273 mmol) of **15**. Recrystallization from $CHCl_3$ gave **15**·$^1/_2CHCl_3$.

Analytical Data for 15. ^1H NMR ($CDCl_3$): δ 1.68 (s, 3 H, CH_3), 1.78 (s, 3 H, CH_3), 1.91 (apparent s, a peak due to unresolved resonances of two Cp* ligands from the two different isomers, 15 H from each isomer), 1.93 (s, 15 H, CH_3 from Cp* of one isomer), 1.94 (s, 3 H, CH_3), 1.96 (s, 15 H, CH_3 from Cp* of one isomer), 1.99 (s, 3 H, CH_3), 2.01 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3), 2.13 (s, 3 H, CH_3), 2.24 (s, 3 H, CH_3), 5.07 (dd, 1 H, J_{cis} = 11.4 Hz, J_{gem} = 1.3 Hz, exo CH=CH*H*), 5.24 (dd, 1 H, J_{cis} = 11.4 Hz, J_{gem} = 1.3 Hz, exo CH=CH*H*), 5.26 (dd, 1 H, J_{trans} = 17.9 Hz, J_{gem} = 1.3 Hz, endo CH=C*H*H), 5.38 (dd, 1 H, J_{trans} = 17.9 Hz, J_{gem} = 1.3 Hz, endo CH=C*H*H), 6.18 (dd, 1 H, J_{cis} = 11.4 Hz, J_{trans} = 17.9 Hz, *CH*=CH_2), 6.60 (dd, 1 H, J_{cis} = 11.4 Hz, J_{trans}

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[26] The use of $CeCl_3$ to activate hindered ketones has been discussed. See: (a) Imamoto, T.; Kusumoto, T.; Tawarayama, Y.; Sugiura, Y.; Hatanaka, Y.; Yokoyama, M. *J. Org. Chem.* **1984**, *49*, 3904. (b) Imamoto, T.; Nakamura, K.; Hatajima, T.; Kamiya, Y. *J. Am. Chem. Soc.* **1989**, *111*, 4392.

= 17.9 Hz, C*H*=CH$_2$). On the basis of differences in integrated intensities, the vinyl proton resonances at δ 5.26, 5.38, and 6.60 were assigned to one isomeric form of **15**, while the resonances at δ 5.07, 5.24, and 6.18 were assigned to the other.

In the ^{13}C{H} NMR spectrum of **15**, twelve resonances are expected in the methyl region of the spectrum ($0 \leq \delta \leq 20$). Only nine of the peaks are cleanly resolved, presumably because several peaks overlap. Two large resonances are observed at δ 10.5 and 11.6. Smaller peaks are observed at δ 9.8, 10.4, 11.1, 11.2, 11.3, 11.9, and 12.3. In the region of the spectrum where the ring carbons of the basal Cp* and C$_5$Me$_4$—CH=CH$_2$ ligands absorb ($104 \leq \delta \leq 107$), twelve resonances are expected, two of which should be relatively large. Eleven peaks are actually observed, of which one is relatively large. On the basis of the relative intensities of the peaks,[27] the largest (δ 105.3) is assigned to overlapping resonances from two Cp* ligands. The other resonances in this region are observed at δ 104.5, 104.7, 105.1, 105.4, 106.0, 106.1, 106.4, 106.7, and 107.0. In the region between δ 115 and 117, resonances due to the ring carbons of the apical Cp* and due to the β-carbon of the vinyl substituent are expected. Peaks at δ 115.0 and 115.8 were assigned to the vinyl carbons of two isomers of **15** on the basis of their appearance as triplets in a separate off-resonance decoupled (ORD) spectrum. A relatively large peak at δ 116.3 (singlet in the ORD spectrum) was assigned to resonances of the apical Cp* ring carbons of the two isomers, which overlap. The α-carbons of the vinyl substituents (doublets in the ORD spectrum) were observed at δ 129.0 and 130.0. Resonances due to the carbonyl carbons were observed at δ 234.4, 235.0, 238.0, 239.0, and 248.0. IR spectrum of **15**: ν_{CO} 1928 (m), 1887 (vs, ϵ = 5.08 L g^{-1} cm^{-1}), 1840 (m), and 1788 cm^{-1} (m). UV/visible (hexane): λ_{max} 632 nm (ϵ = 4390 M^{-1} cm^{-1}). Elemental analysis of **15**·$^1/_2$CHCl$_3$ (Oneida): 48.4% C, 4.9% H, 1.6% N, 5.5% Cl observed; 47.0% C, 5.0% H, 1.5% N, 5.8% Cl expected.

Preparation of (η^5-C$_5$Me$_4$-*p*-C$_6$H$_4$OH)(Cp*)$_2$Mo$_3$(μ_3-N)(O)(CO)$_4$·C$_6$H$_{14}$ (16·hex). A solution which contained 0.469 g (1.00 mmol) of **11** and 1.151 g (2.00 mmol) of **13** was photolyzed in a manner identical to that described for the preparation of **15**. The separation of products was carried out in a manner similar to that described for the preparation of **15**. Elution with 1% (v/v) THF/toluene led to the isolation of a small green band which contained a small amount (0.068 g, 0.070 mmol, 7.0% yield) of (η^5-C$_5$Me$_4$-*p*-C$_6$H$_4$OR)(Cp*)$_2$Mo$_3$(μ_3-N)(O)(CO)$_4$ (**17**, R = CMe$_2$OMe). Subsequent elution of the column with 75% (v/v) THF/toluene led to the isolation of a larger green band. The solvent was removed in vacuo to give a green product which was recrystallized from toluene/hexane to give 0.200 g (0.219 mmol, 21.9% yield) of **16·hex** as a green microcrystalline material.

Analytical Data for 17. IR (CH$_2$Cl$_2$): ν_{CO} 1932 (m), 1884 (vs), 1840 (m), and 1798 cm^{-1} (m).

Analytical Data for 16·hex. ^{1}H NMR (CDCl$_3$): δ 0.88 (m, 6 H, hexane), 1.27 (m, 8 H, hexane), 1.71 (s, 3 H, C*H*$_3$), 1.80 (s, 3 H, C*H*$_3$), 1.88 (s, 3 H, C*H*$_3$), 1.92 (apparent s, a peak due to unresolved resonances of two Cp* ligands from the two different isomers, 15 H from each isomer), 1.96 (s, 15 H, C*H*$_3$ from Cp* of one isomer), 1.97 (s, 15 H, C*H*$_3$ from Cp* of one isomer), 2.00 (s, 3 H, C*H*$_3$), 2.02 (s, 3 H, C*H*$_3$), 2.05 (s, 3 H, C*H*$_3$), 2.08 (s, 3 H, C*H*$_3$), 5.29 (apparent broad s, overlapping O*H* from the two isomers), 6.82 (m, 8 H, overlapping phenyl *H*).

The ^{13}C{H} NMR spectrum of **16** was difficult to obtain because of its poor solubility. A number of the expected peaks were not observed, either due to the low concentration of **16** in our sample, or due to overlapping peaks. In the methyl region of the ^{13}C NMR spectrum ($0 \leq \delta \leq 15$), twelve peaks were expected, four of which should have been relatively large. A total of eight resonances, four of which were relatively large, were observed. The larger resonances (δ 10.4, 10.7, 11.2, and 11.7) were assigned to the methyl carbons of the Cp* ligands. Smaller resonances (δ 10.2, 11.6, 12.5, and 13.0) were assigned to the methyl carbons of the C$_5$Me$_4$-*p*-C$_6$H$_4$OH ligands. For the remaining non-carbonyl carbon atoms, a total of 26 resonances were expected. The observed resonances fell into three clusters. Between δ 105 and 109, two peaks due to the ring carbons of the basal Cp* ligand and eight peaks due to (CMe)$_4$C-*p*-C$_6$H$_4$OH were expected. Only four resonances were resolvable above the noise (δ 105.4, 105.9, 107.7, and 108.6). In the region between δ 114 and 118, two resonances (one from each isomer) due to the apical Cp* ring carbons, two resonances (one from each isomer) due to the phenyl carbon ortho to the OH, and two resonances (one from each isomer) due to (CMe)$_4$C-*p*-C$_6$H$_4$OH were expected. Six of the eight expected resonances were observed above the noise level (δ 114.8, 115.2, 115.6, 116.0, 116.4, and 116.9). In the region between δ 130 and 135, four peaks (two for each isomer) due to the phenyl carbons meta to the OH were expected. Sharp singlets were observed at δ 131.6 and 131.9, and two poorly resolved singlets were observed at ca. δ 132.8. Resonances due to the carbons para to the OH (expected δ ca. 124), the C–OH carbons (expected δ ca. 155), and the carbonyl carbons (expected δ ca. 230–255) were not detected above the noise level.

IR spectrum of **16** (CH$_2$Cl$_2$): ν_{OH} 3580 cm^{-1} (br, m); ν_{CO} 1929 (m), 1884 (vs), 1838 (m), and 1803 cm^{-1} (m). UV/visible spectrum (THF): λ_{max} 634 nm (ϵ = 4460 M^{-1} cm^{-1}).

Copolymerization of Styrene and 5. A Schlenk tube was charged with 0.326 g (1.00 mmol) of **5**, 39.4 mg (0.24 mmol) of AIBN, 50 mL of benzene, and 2.29 mL (20.0 mmol) of styrene. After several freeze–pump–thaw cycles, the Schlenk tube was evacuated and sealed. The resulting mixture was heated at 80 °C for 48 h. After the solution was cooled to room temperature, the volume was reduced to ca. 10 mL in vacuo. Addition of methanol resulted in precipitation of a polymer, which was separated from the mother liquor by filtration. The polymer was purified by three cycles consisting of dissolution in CH$_2$Cl$_2$, followed by addition of methanol and precipitation of the polymer, which was then separated from the mother liquor by filtration. The mother liquor remaining after the last cycle was colorless. A total of 1.033 g of the polymer was isolated.

Analysis of the Styrene–5 Copolymer. IR (CH$_2$Cl$_2$): ν_{CO} 2001 (vs), 1992 cm^{-1} (vs); ν_{NO} 1642 cm^{-1} (vs); $\nu_{polystyrene}$ 1602 cm^{-1} (vs). The metal loading of the polymer was based on a Beer's law analysis using the carbonyl stretches of the polymer-supported organometallic compound and the 1602-cm^{-1} peak of polystyrene (ϵ = 0.221 L g^{-1} cm^{-1}). The apparent molecular weight of the polymer, M_n = 21 000 was determined by the solution viscosity method.[20,21]

Copolymerization of Styrene and 15. A 10-mL round-bottom flask was charged with 3.0 mL of benzene, 33.4 mg (0.0375 mmol) of **15**, and 0.430 mL (3.75 mmol) of styrene. To this solution was added 4.0 μL (0.0094 mmol) of 2.34 M *n*-butyllithium. The mixture was stirred for 20 h. The solution was then concentrated to a volume of ca. 0.5 mL, and methanol was added to quench the reaction and to cause precipitation of the polymer. The supernatant was decanted from the resulting green solid. The polymer was purified by five cycles consisting of dissolution in CH$_2$Cl$_2$, followed by addition of methanol and precipitation of the polymer, which was then separated from the mother liquor by filtration. The mother liquor remaining after the last cycle was colorless.

Analysis of the Styrene–15 Copolymer. IR (CH$_2$Cl$_2$): ν_{CO} 1883 cm^{-1} (vs); $\nu_{polystyrene}$ 1602 cm^{-1} (m). The metal loading of the polymer was based on a Beer's law analysis using the carbonyl stretches of the polymer-supported organometallic compound and the 1602-cm^{-1} peak of polystyrene (ϵ = 0.221 L g^{-1} cm^{-1}). In this preliminary study, no attempt was made to determine the molecular weight of this polymer.

Incorporation of 12·$^1/_2$EtOH into a Preformed Styrene–Maleic Anhydride (sty–mah) Copolymer. A flask was charged with 50 mL of THF, 1.65 g of poly(sty–mah), 0.170 g (0.41 mmol) of **12**·$^1/_2$ETOH, and 60.0 mg (0.49 mmol) of 4-(dimethylamino)pyridine. The solution was stirred for 24 h and then concentrated to ca. 10 mL by removal of solvent in vacuo. Addition of hexane resulted in precipitation of the desired polymer, which was separated from the mother liquor by filtration. The polymer was purified by three cycles consisting of dissolution in THF, followed by addition of hexane and precipitation of the

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[27] In general, the relative intensities of the peaks in the ^{13}C{H} NMR spectrum need not be proportional to the number of carbons which give rise to the respective peaks. This is because the nuclear Overhauser effect can enhance peaks of carbons which are coupled to hydrogens and because of the long relaxation times which are generally associated with carbons which are not coupled to hydrogens. In this particular case, we are comparing only quaternary ring carbons which ought to have similar relaxation times. The relative intensities of these particular peaks ought to reflect the approximate number of carbons which give rise to the respective peaks.

polymer, which was separated from the mother liquor by filtration. The mother liquor which remained after the last cycle was colorless.

Analysis of the sty–mah-12 Copolymer. IR (THF): ν_{CO} 2002 (vs), 1925 cm^{-1} (vs); ν_{NO} 1649 cm^{-1} (vs); $\nu_{polystyrene}$ 1602 cm^{-1} (m). The metal loading of the polymer was determined by a Beer's law analysis using the carbonyl stretches of the polymer-supported organometallic compound and the 1602-cm^{-1} peak of poly(sty–mah) (ϵ = 0.111 L g^{-1} cm^{-1}).

Incorporation of 16·hex into a Preformed Styrene–Maleic Anhydride (sty–mah) Copolymer. A flask was charged with 30 mL, THF, 0.8711 g of poly(sty–mah), 40.1 mg (0.040 mmol) of 16·hex, and 6.0 mg (0.049 mmol) of 4-(dimethylamino)pyridine. The solution was stirred for 24 h and then concentrated to ca. 10 mL by removal of solvent in vacuo. Addition of hexane resulted in precipitation of the desired polymer, which was separated from the mother liquor by filtration. The polymer was purified by three cycles consisting of dissolution in THF, followed by addition of hexane and precipitation of the polymer, which was separated from the mother liquor by filtration. The mother liquor which remained after the last cycle was colorless.

Analysis of the sty–mah-16 Copolymer. UV/vis (THF): λ_{max} = 628 nm. Beer's law analysis of the polymer utilizing the 628-nm absorbance of the cluster indicated that the polymer contained 0.64 mol % **16**.

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Notes

Regioselective Reduction Reactions of the Cationic Benzene Complex (η^6-C_6H_6)RuCl($Cy_2PCH_2CH_2PCy_2$)$^+$

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Summary: The new cationic ruthenium(II) complex [(η^6-C_6H_6)RuCl($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3 has been prepared by treating [(η^6-C_6H_6)$RuCl_2$]$_2$ with $Cy_2PCH_2CH_2PCy_2$ and $AgCF_3SO_3$. This cationic complex reacts with sodium/potassium alloy to give the ruthenium(0) complex (η^6-C_6H_6)Ru($Cy_2PCH_2CH_2PCy_2$) and with $NaBH_4$ or $LiAlH_4$ to give [(η^6-C_6H_6)RuH($Cy_2PCH_2CH_2PCy_2$)]CF_3SO_3 and (η^5-C_6H_7)RuH($Cy_2PCH_2CH_2PCy_2$), respectively.

η^6-Arene complexes of ruthenium(II) have been studied by several different groups of researchers.[1] These complexes have attracted interest because they represent one of the few examples of a series of stable η^6-arene complexes of a transition metal which are amenable to isolation in high yield. The particular group of complexes which are relevant to this work are those of type (η^6-arene)$RuXL_2^+$ (X = anionic ligand; L = tertiary phosphine), which have a piano-stool structure.[2] These complexes have been shown to undergo two-electron reduction to the ruthenium(0) complex (η^6-arene)RuL_2.[3] Alternately, these cationic complexes, like those of other transition metals, can undergo nucleophilic attack at the η^6-arene ligand to give a η^5-cyclohexadienyl complex.[4] When the nucleophile is hydride, an alternate possibility is that attack can occur at the metal center rather than at the benzene ring to give a ruthenium hydride product.[5] In this paper we report the synthesis of the new cationic complex (η^6-C_6H_6)RuCl($Cy_2PCH_2CH_2PCy_2$)$^+$, and report the selectivity of its reduction chemistry. We find that it is possible to choose reagents either to effect selectively its reduction to a ruthenium(0) complex, to achieve hydride ion coordination to the ruthenium(II) center by chloride ion substitution, or to effect hydride ion transfer to *both* the ruthenium(II) center and the complexed η^6-arene. Results are presented that show a parallel with those found for (η^6-C_6H_6)Mn(CO)$_3^+$.[6]

Experimental Section

The complex [(η^6-C_6H_6)$RuCl_2$]$_2$ was prepared by standard procedures. The compound 1,2-bis(dicyclohexylphosphino)ethane was purchased from Strem Chemicals. Hydrated ruthenium trichloride was supplied by Matthey Bishop Corp., Malvern, PA. Silver trifluoromethanesulfonate was purchased from Aldrich Corp. Sodium borohydride and lithium aluminum hydride were commercial samples, and sodium/potassium alloy was prepared by standard procedures. Solvents were dried by standard techniques, and NMR spectra were measured in C_6D_6. All reactions were carried out either in a Vacuum Atmospheres drybox or by using cannula techniques. The NMR spectra were run on a Bruker AC200 or on a GE Omega 400 spectrometer. Microanalyses were carried out by Galbraith Inc., Knoxville, TN.

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