Syntheses and Characterization of the First Cycloheptatrienyl Transition-Metal Complexes with a M-CF₃ Bond

Christos Lampropoulos 1,2,3, Gabriel Rashad 4 and Chris Douvris 4,*

1 DrL Consultations, Jacksonville, FL 32257, USA; DrL.Consultations@gmail.com
2 Florida State College at Jacksonville, Jacksonville, FL 32202, USA
3 James Weldon Johnson MS, Duval County Public Schools, Jacksonville, FL 32207, USA
4 Theobald Science Center, Department of Biological and Chemical Sciences, New York Institute of Technology, Old Westbury, NY 11568, USA; grashad@nyit.edu
* Correspondence: cdouvris@nyit.edu; Tel.: +1-516-686-1202

Abstract: The organometallic chemistry of metal complexes with organocyclic ligands of higher than five hapticity is much more lacking than the chemistry of metal complexes with η⁵-cyclopentadienyl ligands, which has been explored in considerable depth, resulting in novel advances. The main reason for this is stability. In particular, reports indicate that (η⁵-C₇H₅)ML₅ complexes are considerably less stable than analogous (η⁵-C₇H₅)ML₆ complexes. In perfluoroalkyl metal chemistry, there is currently no reported (η⁵-C₇H₅)ML₆ derivative, whereas a number of alkylated ones are known and important conclusions have been drawn about their stability. Responding to this void, and using Morrison’s trifluoromethylation reagent, the present study reports the synthesis and characterization of the first cycloheptatrienyl molybdenum complexes bearing the trifluoromethyl moiety; (η⁵-C₇H₅)Mo(CO)₂CF₃ (I), and (η⁵-C₇H₅)Mo(CO)(PMe₃)CF₃ (II) and discusses their low thermal instability.

Keywords: trifluoromethyl group; molybdenum complexes; cycloheptatrienyl ligand

1. Introduction

The interest in the chemistry of the trifluoromethyl group is both theoretical and industrial as the demand for compounds containing CF₃ moieties is high due to their applications in advanced materials, pharmaceuticals, agrochemicals, fluorous chemistry, and medicine [1,2]. In organometallic chemistry, despite the interest, the number of transition metal complexes bearing perfluoroalkyl ligands is small. This is especially evident if their number is compared with the that of the alkyl counterparts [3]. The plethora of known alkylated transition metal complexes and the efficiency of their preparation methods has made possible several extremely important advances in both theoretical and practical application chemistry of the C-H bond, with most notable being the study of C-H activation using transition metal catalysts [4,5]. Parallel to this, similar advances in the perfluoroalkyl chemistry could be envisioned with establishing efficient routes for transition metal alkylated complexes [6,7].

With a focus on the trifluoromethyl group, the most important of fluorocarbons, we set out to explore the synthesis and characterization of trifluoromethylated metal complexes with the metal having hapticity greater than five. It is well known that systems of (η⁵-C₇H₅)ML₅ (M = transition metal, L₅ = n-ligands) are ubiquitous in organometallic chemistry and as reports suggest of much higher stability than analogous systems with carboxyclic ligands of with higher hapticity, such as (η⁵-C₇H₅)ML₆ [8]. An illustrative example is the (η⁵-C₇H₅)Mo(CO)₂CH₃, which chromatography is at −78 °C for its isolation, and it is reported to rapidly decompose even under inert atmosphere at ambient temperature [9]. In contrast to this, the complex (η⁵-C₇H₅)Mo(CO)₃CH₃ is indefinitely air stable and melts at 145 °C without decomposition [10,11].
Trifluoromethyl metal complexes are predicted to be more stable than their methylated counterparts, as the back donation from the π* orbital increases the strength to the metal to carbon bond [3]. Considering this fact, as well as the intriguing instability of the reported methylated η7-cycloheptatrienyl complexes, we set out to explore the synthesis and stability of analogous trifluoromethylated species. As a result, we report herein the synthesis and characterization of the first η7-cycloheptatrienyl trifluoromethyl molybdenum complexes, (η7−C7H7)Mo(CO)2CF3 (I) and (η7−C7H7)Mo(CO)(PMe3)CF3 (II). As we will describe, the two new complexes are of extreme thermal instability, a fact that necessitates the use of low temperature chromatography for their purification.

2. Results

Upon choosing (η7−C7H7)Mo(CO)2I as the precursor for the trifluoromethylation reaction, this was initially reacted with a number of nucleophilic trifluoromethylating reagents, including CF3I/Cu in DMF, which is known to generate CuCF3 in situ [12], and (CH3)3SiCF3/AgF, which is known to generate AgCF3 in situ [13], at ambient and elevated temperatures; however, no formation of a Mo-CF3 bond was observed, as monitored by 19F NMR spectroscopy. In a reaction maintained at −20 °C between (η7−C7H7)Mo(CO)2I, and Morrison’s reagent, Cd(CF3)2(DME), (DME = dimethoxyethane), a resonance at δ = −0.2 ppm, indicative of a Mo-CF3 bond, slowly appeared in the 19F NMR spectrum. However, the yield of the product as it was measured in respect to an C6H5CF3 internal standard, was less than 5%. As the reaction progressed, the product peak along with the one of Cd(CF3)2(DME), δ = −37.0 ppm, JF-Cd(111) = 454 Hz, JF-Cd(113) = 472 Hz, disappeared, giving rise to resonances at δ = −80.0 ppm assigned to CF3H (JF-H = 78 Hz), and δ = −134.9 ppm, assigned to C2F4, indicating decomposition. The reaction yield was 10%, which was subsequently improved, albeit not significantly, when carefully dried CuBr was added to the reaction mixture (Scheme 1). Attempts to isolate the new (η7−C7H7)Mo(CO)2CF3 (I) with ambient temperature workup failed, and finally complex I was obtained at 17% yield by purification at −20 °C. Complex I is stable under inert atmosphere for a few minutes. It also decomposes rapidly when in solution at temperatures higher than −20 °C.

![Scheme 1. Synthesis of complexes I and II.](image-url)

As substitution of a CO by a PMe3 ligand is known to enhance the stability of a metal complex [5], the synthesis of the (η7−C7H7)Mo(CO)(PMe3)CF3 was targeted next. The new (η7−C7H7)Mo(CO)(PMe3)I (III) was synthesized, characterized, and served as a precursor for a similar to the aforementioned trifluoromethylation reaction using Cd(CF3)2(DME)/CuBr (Scheme 1). The reaction mixture was always maintained at −10 °C, and after workup in a chromatography column at the same temperature, complex II was isolated as a dark green
solid. Upon isolation, complex II is stable in air for only a few minutes, and stable under inert atmosphere for a few hours. Our experiments indicated that II decomposes rapidly, when in solution at room temperature, or when the workup is attempted at temperatures higher than −10 °C.

Complex II, fluorine-to-phosphorus coupling constants, $J_{F-P}$, are reported for the first time for cycloheptatrienyl complexes. In particular, the $^{31}$P NMR chemical shift of $(\eta^7$-$C_7H_7$)Mo(CO)(PMe$_3$)CF$_3$ registers as a quartet as the $^{31}$P nucleus interacts with three $^{19}$F nuclei, with $^3J_{F-P} = 8.3$ Hz. The same value is recorded for the $^3J_{F-P}$ of in the $^{19}$F NMR for the doublet observed for complex II (Figure 1).

![Figure 1](image-url)

Figure 1. The $^{19}$F NMR (a) and $^{31}$P NMR (b) of complex II. Refer to the text for the analysis of the peaks and their ppm values.

3. Discussion

Trifluoromethyl derivatives of low-valent, late transition metal complexes are known to be more thermally and oxidatively stable than the analogous methylated species. This is believed to be due to back-bonding from the metal d orbitals into the unoccupied C-F antibonding orbitals; this bonding type is not available for M-CH$_3$ analogues. However, making similar arguments for early transition metals is problematic due to insufficient data. Considering the interest in the chemistry of the CF$_3$ group [14,15], as well as the intriguing instability of previously reported, methylated $\eta^5$-cycloheptatrienyl complexes, we set out to explore the synthesis, preparation, and stability of analogous trifluoromethyl species for the first time.

An additional consideration that makes the exploration of the newly synthesized complexes attractive is the fact that the chemistry of complexes containing carbocyclic rings of higher than five hapticity is largely overlooked, most likely due to their higher instability compared to the reported stability of other cyclopentadienyl derivatives. For example, the thermal instability of the aforementioned $(\eta^7$-$C_7H_7$)Mo(CO)$_2$CH$_3$ complex is in stark contrast to the high stability of the closely related $(\eta^5$-$C_5H_5$)Mo(CO)$_3$CH$_3$, which is reported to be indefinitely stable at room, as well as elevated, temperatures, and can melt without decomposition.

Even though routes to L$_n$MCH$_3$ complexes are well-established, utilizing highly efficient, commercially available reagents, such as CH$_3$Li and CH$_3$MgBr, for the synthesis [16], analogous routes to of L$_n$MCF$_3$ derivatives are not straightforward as it is not similarly efficient and easy to access trifluoromethyllating reagents. This results in relatively small L$_n$MCF$_3$ complexes compared with L$_n$MCH$_3$ ones [16].

Complex I appears to be more thermally stable than its methyl counterpart $(\eta^7$-$C_7H_7$)Mo(CO)$_3$CH$_3$, as an isolated solid and as its workup is performed at much higher temperatures. This fact can be explained by the stabilization of the Mo-C bond resulting
from the back donation of the \( \pi^* \) orbital of the trifluoromethyl group. As it has been previously indicated, the substitution of a trifluoromethyl group for a methyl group increases the thermal stability of low valent transition metal complex by raising the decomposition temperature of the perfluorinated derivatives by 75–100 °C. An illustrative literature example is the trifluoromethyl cobalt derivative \( \text{CF}_3\text{Co(CO)}_4 \), which does not decompose when heated to 90°, whereas the \( \text{CH}_3\text{Co(CO)}_4 \) decomposes near −35 °C [3]. Regardless the increased stability, complexes I and II are shown to still be highly thermally unstable, especially when they compared (in a similar manner that the methyl analogs are compared) with the closely related known, cyclopentadienyl complexes, \((\eta^5\text{C}_5\text{H}_5)\text{Mo(CO)}_2\text{CF}_3\) and \((\eta^5\text{C}_5\text{H}_5)\text{Mo(CO)}_2(\text{PMe}_3)\text{CF}_3\). The \( \text{C}_5\text{H}_5\text{-Mo} \) complexes are highly stable both in the solid form and in solution, with the former reported not to decompose for two years in the absence of light. Comparison of the IR C-O stretches (2020 and 1937 cm\(^{-1}\)) for the \((\eta^5\text{C}_5\text{H}_5)\text{Mo(CO)}_3\text{CF}_3\) vs. 2007, 1953 cm\(^{-1}\) for the \((\eta^7\text{-C}_7\text{H}_7)\text{Mo(CO)}_2\text{CF}_3\) may suggest that the cycloheptatrienyl ligand may donate more electron density than the \( \eta^5\text{C}_5\text{H}_5 \) ligand through the Mo center into the \( \pi^* \) orbitals of the carbonyl and trifluoromethyl ligands, in a manner of making the trifluoromethyl group of complex I, weaker, and thus more reactive than the trifluoromethyl group of \((\eta^5\text{C}_5\text{H}_5)\text{Mo(CO)}_3\text{CF}_3\). This is consistent with the formal charges of \( \text{C}_7\text{H}_7^+ \) and \( \text{C}_5\text{H}_5^- \) [8]. Nevertheless, the latter and complex I differ not only in terms of the carbocyclic group, but also by the fact that I has one less carbonyl substituent, a fact that makes unclear the direct comparison of the effect of the carbocyclic group on the M-CF\(_3\) bond.

Comparison of the stability of complexes I and II indicates that the phosphine analog is more stable than the di-carbonyl one, a trend which has been previously reported for methylated molybdenum derivatives.

Conclusively, the preparation of the first cycloheptatrienyl molybdenum complexes with a M-CF\(_3\) bond can lead to useful insights of the behavior of the trifluoromethyl group in these environments by future reactivity as well as structural studies, similar to the ones that have been conducted for the methylated analogs.

4. Materials and Methods

All reactions and manipulations were performed in oven- or flame-dried glassware under nitrogen atmosphere, either in a glovebox or by using standard Schlenk techniques. Column chromatography was carried out using silica gel 62 (60–200 mesh) supplied by Mallinckrodt SilicaAR (Mallinckrodt Pharmaceuticals, Staines-upon-Thames, UK) which had been pre-dried at 250 °C under high vacuum. Furthermore, 1,2-dimethoxyethane (DME), diethyl ether (Et\(_2\)O) and toluene (C\(_6\)H\(_5\)CH\(_3\)) were distilled from sodium-benzophenone ketyl under N\(_2\) atmosphere. Hexanes (C\(_6\)H\(_12\)) and C\(_6\)D\(_6\) were distilled from sodium (Na). Dichloromethane (CH\(_2\)Cl\(_2\)) and d-chloroform (CDCl\(_3\)) were dried over calcium hydride (CaH\(_2\)) and distilled under nitrogen prior to use. Copper bromide (CuBr) was purchased from Aldrich and dried by heating to 45 °C for 12 h under high vacuum. Trimethylphosphine (PMe\(_3\)) was purchased from Aldrich and used as received.

(C\(_7\)H\(_7\))Mo(CO)\(_2\)I, and Cd(CF\(_3\))\(_2\)(DME), were prepared and purified by literature methods [17,18].

The \(^1\)H NMR, \(^{13}\)C NMR, \(^{31}\)P NMR, and \(^{19}\)F NMR spectra were recorded on a Bruker either DRX 400 or DRX 500 spectrometers with Nalorac BB probes. All \(^1\)H chemical shifts are reported in ppm (\( \delta \)) relative to SiMe\(_4\). \(^{19}\)F NMR and \(^{31}\)P NMR chemical shifts are given in ppm upfield from CFCl\(_3\) and H\(_3\)PO\(_4\) (85% aqueous solution), respectively. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet). Coupling constants are reported in Hertz (Hz). Infrared spectra (IR) were recorded on an ATI Mattson Genesis Series FTIR spectrometer and are given in cm\(^{-1}\). LRMS-EI were also obtained on a Hewlett Packard 5987A quadrupole instrument. HRMS analyses were performed using a Finnigan LCQ spectrometer in the APCI mode. Elemental combustion analyses were performed by Midwest Microlab, LLC of Indianapolis, IN, USA.
Syntheses of \((\eta^2-C_7H_7)Mo(CO)_2(\text{CF}_3)\) (I) \((\eta^2-C_7H_7)Mo(CO)_2\) (50 mg, 0.135 mmol), Cd(\text{CF}_3)_2(DME) (92 mg, 0.270 mmol) and CuBr (40 mg, 0.279 mmol) were loaded into a 10 mL round bottom flask and the apparatus was attached to a vacuum line. It was then cooled to \(-196^\circ\text{C}\) and evacuated. Anhydrous DME (4 mL) was condensed into the flask and the reaction mixture was allowed to reach \(-20^\circ\text{C}\) with stirring. After 5 h at that temperature, the reaction flask was opened, and the contents were filtered. The filtrate was chromatographed at \(-20^\circ\text{C}\), on an alumina column \((15 \times 1 \text{ cm})\) using dry diethyl ether as eluent. A green fraction was collected, its volume was reduced to about 1 mL. Hexanes (8 mL) were added, and the solution was placed in a \(-78^\circ\text{C}\) bath for 2 h, to precipitate a yellow-green solid identified as I \((7 \text{ mg}, 0.022 \text{ mmol}, 16\% \text{ yield})\). \(^1\text{H}\) NMR (6 ppm, in CDCl$_3$): 1.53 (d, 9H, \(\text{P(CH}_3\text{)}_3\), \(3\text{J}_{\text{P-H}} = 8 \text{ Hz}\)); 5.15 (s, 7H, \(\text{C}_7\text{H}_7\))\(^{13}\text{C}\) NMR (6 ppm in CDCl$_3$): 19.8 (d, 3C, \(\text{P(CH}_3\text{)}_3\), \(1\text{J}_{\text{C-P}} = 27 \text{ Hz}\)), 90.7 (s, 7C, \(\text{C}_7\text{H}_7\)); \(^{31}\text{P}\)\(^{1}\text{H}\) NMR (6 ppm in CDCl$_3$): 30.9 (s, 1P, \(\text{P(CH}_3\text{)}_3\)). FT-IR (cm$^{-1}$, KBr pellet) 1997, 1945 (C-O), LRCl-MS (m/e, ion, %): \((\text{C}_7\text{H}_7)\)Mo(CO)(PMe$_3$)I, 418, 23; \((\text{C}_7\text{H}_7)\)Mo(PMe$_3$)I, 390, 10; \((\text{C}_7\text{H}_7)\)Mo(CO)(PMe$_3$)I, 342, 29; \((\text{C}_7\text{H}_7)\)Mo, 314, 19; \((\text{C}_7\text{H}_7)\)Mo, 187, 69, \((\text{C}_7\text{H}_7)\), 91, 100. Measured HRCl-MS m/z: 419.9151, Calculated: 419.9037 \((\Delta \text{ m/m} = 2.7 \text{ ppm})\). Elemental Analysis: Found: C 31.39, H 3.88. Calc: C 31.60, H 3.86.

Syntheses of \((\eta^2-C_7H_7)Mo(CO)(\text{PMe}_3)\text{CF}_3\) (II) \((\eta^2-C_7H_7)\)Mo(CO)(PMe$_3$)I (30 mg, 0.072 mmol), Cd(\text{CF}_3)$_2$(DME) (40 mg, 0.117 mmol), and CuBr (30 mg, 0.209 mmol) were loaded into a 10 mL round bottom flask and the apparatus was attached to a vacuum line. It was cooled to \(-196^\circ\text{C}\) and evacuated. Anhydrous DME (4 mL) was condensed into the flask and the reaction mixture was allowed to reach \(-10^\circ\text{C}\) with stirring. After 5 h at that temperature, the reaction flask was opened, and the contents were filtered. The filtrate was chromatographed at \(-10^\circ\text{C}\), on an alumina column \((15 \times 1 \text{ cm})\) using Et$_2$O as eluent. A green fraction was collected, and its volume was reduced to 1 mL. Hexanes (8 mL) were added, and the solution was placed in a \(-78^\circ\text{C}\) bath for 2 h, to precipitate a yellow-green solid identified as II \((14 \text{ mg}, 0.039 \text{ mmol}, 54\% \text{ yield})\). \(^1\text{H}\) NMR (6 ppm, in CDCl$_3$): 1.47 (d, 9H, \(\text{P(CH}_3\text{)}_3\), \(3\text{J}_{\text{P-H}} = 7 \text{ Hz}\)); 5.13 (s, 7H, \(\text{C}_7\text{H}_7\))\(^{13}\text{C}\) NMR (6 ppm in CDCl$_3$): 18.6 (d, 3C, \(\text{P(CH}_3\text{)}_3\), \(1\text{J}_{\text{C-P}} = 24 \text{ Hz}\)), 90.9 (s, 7C, \(\text{C}_7\text{H}_7\)); \(^{31}\text{P}\)\(^{1}\text{H}\) NMR (6 ppm in CDCl$_3$): \(-6.3 \text{ (q, 1P, P(CH}_3\text{)}_3, 3\text{J}_{\text{P-F}} = 8.3 \text{ Hz})\); \(^{19}\text{F}\) NMR (6 ppm, in C$_6$D$_6$): \(-3.2 \text{ (d, 3F, CF}_3, 3\text{J}_{\text{F-P}} = 8.3 \text{ Hz})\). FT-IR (cm$^{-1}$, KBr pellet) 2020 (C-O), 1054, 1077 (C-F). Elemental Analysis: Found: C 40.62, H 5.49. Calc: C 40.02, H 4.48.

Author Contributions: Conceptualization, C.D.; synthesis, data collection, C.L., G.R., C.D.; writing—original draft preparation, C.L. and C.D.; writing—review and editing, G.R and C.D.; funding acquisition, C.D. All authors have read and agreed to the published version of the manuscript.

Funding: We are grateful to the New York Institute of Technology for financial support for this research.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data reported herein are accompanying the present article.

Conflicts of Interest: The authors declare no conflict of interest.
References

1. Yale, H.L. The Trifluoromethyl Group in Medical Chemistry. *J. Med. Pharm. Chem.* 1959, 1, 121–133. [CrossRef] [PubMed]

2. Barthel-Rosa, P.L.; Gladysz, A.J. Chemistry in Fluorous Media: A User’s Guide to Practical Considerations in the Application of Fluorous Catalysts and Reagents. *Coord. Chem. Rev.* 1999, 190, 587–605. [CrossRef]

3. Morrison, J.A. Trifluoromethyl-Containing Transition Metal Complexes. *Adv. Organomet. Chem.* 1993, 35, 211–239.

4. Bergman, R.G. C–H Activation. *Nature* 2007, 446, 391–393. [CrossRef] [PubMed]

5. Robert, H. Crabtree. In *The Organometallic Chemistry of the Transition Metals*; Wiley: Hoboken, NJ, USA, 2019.

6. Douvris, C. Synthesis and Characterization of the First η^5-Arene Trifluoromethyl Transition-Metal Complex. *J. Fluor. Chem.* 2021, 245, 109755. [CrossRef]

7. Guillevic, M.-A.; Rocaboy, C.; Arif, A.M.; Horváth, I.T.; Gladysz, J.A. Organometallic Reactivity Patterns in Fluorocarbons and Implications for Catalysis: Synthesis, Structure, Solubility, and Oxidative Additions of a Fluorous Analogue of Vaska’s Complex, Trans -Ir(CO)(Cl)[P(CH_2CH_2CF_2CF_3)_2]. *Organometallics* 1998, 17, 707–717. [CrossRef]

8. Green, M.L.H.; Ng, D.K.P. Cycloheptatriene and -Enyl Complexes of the Early Transition Metals. *Chem. Rev.* 1995, 95. [CrossRef]

9. Schulze, W.; Ziegler, M.L. Darstellung Und Charakterisierung von Wolframkomplexen Mit ER^-Liganden; E = O, S, Se, Te; R = Alkyl, Aryl. *Z. Fur Anorg. Und Allg. Chem.* 1981, 481, 78–94. [CrossRef]

10. King, R.B. *Organometallic Syntheses*; Academic Press: New York, NY, USA, 1965; Volume 1.

11. Beletskaya, I.P.; Sazonov, P.K. *E-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley: Hoboken, NJ, USA, 2013.

12. Matsui, K.; Tobita, E.; Ando, M.; Kondo, K. A Convenient Trifluoromethylation of Aromatic Halides with Sodium Trifluoroacetate. *Chem. Lett.* 1981, 10, 1719–1720. [CrossRef]

13. Wang, X.; Xu, Y.; Mo, F.; Ji, G.; Qiu, D.; Feng, J.; Ye, Y.; Zhang, S.; Zhang, Y.; Wang, J. Silver-Mediated Trifluoromethylation of Aryldiazonium Salts: Conversion of Amino Group into Trifluoromethyl Group. *J. Am. Chem. Soc.* 2013, 135, 10330–10333. [CrossRef]

14. Prakash, G.K.S.; Richard, D.C.; Olah, G.A. *Synthetic Fluorine Chemistry*; Wiley: Hoboken, NJ, USA, 1992.

15. Purser, S.; Moore, P.R.; Swallow, S.; Gouverneur, V. Fluorine in Medicinal Chemistry. *Chem. Soc. Rev.* 2008, 37, 320–330. [CrossRef] [PubMed]

16. Daniels, A.; da Gama, J.; Edjoc, R.; Gabidullin, B.; Baker, R. Synthesis and Reactivity of Mn–CF_3 Complexes. *Inorganics* 2019, 7, 3. [CrossRef]

17. El-Tarhuni, S.; Ho, M.; Kawser, M.H.; Shi, S.; Whiteley, M.W. Synthesis and Solvent Induced Halide Exchange of the Electron Rich, Half Sandwich Complexes [Fel(Dppe)Cp] and [MoX(Dppe)(η^7-C_7H_7)] (X = Br, Cl; Dppe = Ph2PCH2CH2PPh2). *J. Organomet. Chem.* 2014, 752, 30–36. [CrossRef]

18. Loizou, D.C.; Castillo, J.; Oki, A.R.; Hosmane, N.S.; Morrison, J.A. Synthesis of Cyclopentadienyldinitrosyl(Trifluoromethyl)Chromium(0), CpCr(NO)_2CF_3, and Cyclopentadienyldinitrosyl(Trifluoromethyl)Molybdenum(0), CpMo(NO)_2CF_3. *Crystal Structure of CpCr(NO)_2CF_3. Organometallics* 1992, 11, 4189–4193. [CrossRef]