Synthesis of Bis(η^6-alkylbenzene)molybdenum by Arene Metathesis

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Received November 27, 2000

Summary: Bis(η^6-arene)molybdenum complexes with alkyl substituents are readily synthesized by metathesis of the arene ligands of bis(η^6-benzene)molybdenum, thereby circumventing a fundamental limitation of the conventional Fischer−Hafner syntheses (Friedel−Crafts conditions) and obviating the need to employ metal-vapor synthetic methods to prepare such compounds.

Introduction

Since the first report of (η^6-C_6H_6)$_2$Mo by Fischer and Stahl in 1956,[1] many routes have been employed to synthesize bis(η^6-arene)molybdenum complexes.[2] Scheme 1 illustrates the Fischer−Hafner synthesis[3,4] (FHS) of (η^6-C_6H_6)$_2$Mo, which may be accomplished using conventional Schlenk techniques in good yield (27−72%).[5] A severe limitation of the FHS method is that it cannot be applied to aromatics that are themselves reactive under Friedel−Crafts conditions. Accordingly, the FHS has proven useful only for the preparation of two methyl benzene derivatives of bis(η^6-arene)molybdenum (toluene and mesitylene). The metal-vapor synthesis (MVS) technique[6] affords a milder method of synthesis, and it has been employed to prepare a variety of bis(η^6-arene)-molybdenum complexes by (1) direct condensation of Mo vapor and aromatics (10−50%)[7] and (2) condensation of K vapor into a solution containing $MoCl_5$ and the aromatic in THF at −100 °C (40−45%).[8] However, the equipment necessary to employ MVS is not routinely available and the MVS reactions are generally carried out on a smaller scale than FHS. We report herein that (η^6-C_6H_5R)$_2$Mo for R = Et, Pr^i, and Bu^t are readily synthesized from (η^6-C_6H_6)$_2$Mo in high yield by arene metathesis.

Results and Discussion

Alkyl groups are cleaved from aromatic rings in the presence of Lewis acids in the order primary < secondary < tertiary.[9] Indeed, *tert*-butyl groups are often introduced into aromatics for their directing abilities to later be cleaved by $AlCl_3$.[10] Mixtures of various isomers of alkyl and dialkyl bis(η^6-arene)molybdenum complexes are generally obtained if alkylbenzenes are employed in the FHS. The only exceptions to this rule are toluene[11] and mesitylene.[12] Thus, a mixture of (η^6-C_6H_6)-(η^6-C_6H_5Et)Mo, (η^6-C_6H_5Et)$_2$Mo, (η^6-C_6H_5Et)(η^6-$C_6H_4Et_2$)Mo, and (η^6-$C_6H_4Et_2$)$_2$Mo is obtained when ethylbenzene is employed in the FHS.[13] It is well recognized that the arene ligands of (η^6-C_6H_6)$_2$Mo are relatively labile, a property that makes the compound useful in the synthesis of half-sandwich complexes.[2,14−16] To explore whether this property could be exploited to synthesize bis(η^6-arene)molybdenum complexes that are not readily prepared using the FHS, we have studied the solution properties of (η^6-C_6H_6)$_2$Mo in the aromatic solvents ethylbenzene, isopropylbenzene, and *tert*-butylbenzene.[17] These solvents replace the coordinated benzene of (η^6-C_6H_6)$_2$Mo at elevated temperatures to cleanly produce the corresponding bis(η^6-alkylbenzene)-molybdenum complexes in 60−70% yield.

Bis(η^6-alkylbenzene)molybdenum complexes have up to now only been obtainable vis-à-vis MVS approaches, either directly via co-condensation of molybdenum atoms and an alkylbenzene or indirectly via reaction of alkyllithium reagents with bis(η^6-chlorobenzene)molybdenum (which is itself synthesized by MVS).[18] The procedure outlined herein offers a high-yield alternate route that employs conventional equipment.

Experimental Section

General Information. All operations were carried out using Schlenk or glovebox techniques under argon or nitrogen. Hydrocarbon solvents were distilled from sodium/benzophenone ketal. (η^6-C_6H_6)$_2$Mo was synthesized according to pub-

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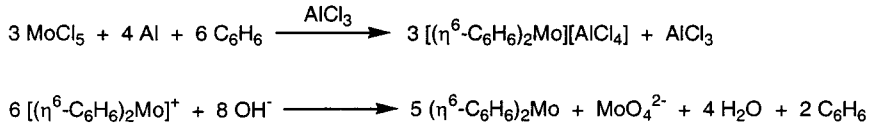
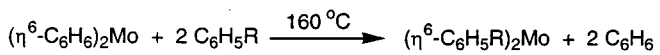
10.1021/om001010b CCC: $20.00
Publication on Web 03/15/2001

Scheme 1

Fischer-Hafner Synthesis



Arene Metathesis



lished procedure.[5] ^{1}H NMR spectra were recorded on a Varian XL-500 spectrometer. The NMR samples were prepared in tubes that had been glass-blown onto Schlenk adapters. The solutions were freeze−pump−thawed before the tubes were flame-sealed under vacuum. ^{1}H NMR spectra were referenced to residual C_6D_5H (7.24 ppm).

General Procedure for the Synthesis of (η^6-$C_6H_5R)_2Mo$ (R = Et, Pr^i, and Bu^t). In a typical reaction, (η^6-$C_6H_5)_2Mo$ (100 mg, 0.4 mmol) and the aromatic (2 mL) were added to a Schlenk flask, the solution was frozen and evacuated, and the flask was sealed under vacuum and placed in a 160 °C oil bath for 48 h. Hotter temperatures result in significant decomposition. Excess solvent was removed by vacuum transfer, and the product was recrystallized or sublimed. Purity was assessed by ^{1}H and ^{13}C NMR and FAB mass spectrometry. Typical isolated yields were 60−70%. (η^6-$C_6H_5CH_2CH_3)_2Mo$: ^{1}H NMR (C_6D_6, 500 MHz, 20 °C) δ 4.57 (m, 5 H, $C_6H_5CH_2CH_3$), 2.05 (q, 2 H, $J_{HH} = 7$ Hz, $C_6H_5CH_2CH_3$), 1.02 (t, 3 H, $J_{HH} = 7$ Hz, C_6H_5-CH_2CH_3); ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 20 °C) δ 97.5 (*ipso*), 77.7 (*ortho*), 76.0 (*para*), 75.2 (*meta*), 29.6 ($-CH_2-$), 16.9 ($-CH_3$). (η^6-$C_6H_5CH(CH_3)_2)_2Mo$: ^{1}H NMR (C_6D_6, 500 MHz, 20 °C) δ 4.52 (m, 5 H, $C_6H_5CH(CH_3)_2$), 2.20 (sept, 1 H, $J_{HH} = 7$ Hz, $C_6H_5CH(CH_3)_2$), 1.08 (d, 6 H, $J_{HH} = 7$ Hz, $C_6H_5CH(CH_3)_2$); ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 20 °C) δ 103.5 (*ipso*), 76.3 (*ortho*), 75.9 (*para*), 75.2 (*meta*), 34.2 ($-CH-$), 25.0 ($-CH_3$). (η^6-$C_6H_5C(CH_3)_3)_2Mo$: ^{1}H NMR (C_6D_6, 500 MHz, 20 °C) δ 4.52 (m, 5 H, $C_6H_5C(CH_3)_3$), 1.12 (s, 9 H, $C_6H_5C(CH_3)_3$); ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz, 20 °C) δ 106.9 (*ipso*), 75.5 (*ortho*), 75.4 (*para*), 75.2 (*meta*), 34.4 ($-C(CH_3)_3$), 32.0 ($-C(CH_3)_3$).

Acknowledgment. The financial support of the National Science Foundation (CHE-9612869) and the Oklahoma Center for the Advancement of Science and Technology (OCAST HR98-078) is gratefully acknowledged.

OM001010B