12. BIS(η^5 -PENTAMETHYLCYCLOPENTADIENYL) COMPLEXES OF MOLYBDENUM

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Molybdenocene and tungstenocene complexes have played a prominent role in the development of organometallic chemistry. By comparison to the parent molybdenocene and tungstenocene systems, however, the chemistry of permethylmolybdenocene and permethyltungstenocene complexes has been little explored. With respect to the permethylmolybdenocene system, the first report of the dihydride (η^5 -C₅Me₅)₂MoH₂ and several other derivatives appeared in 1973,¹ but there were no subsequent reports until 1991 when Cloke synthesized (η^5 -C₅Me₅)₂MoH₂ by using metal vapor synthesis techniques.² The paucity of studies pertaining to (η^5 -C₅Me₅)₂MoH₂ may be attributed to the inability of other researchers to substantiate the 1973 synthesis of (η^5 -C₅Me₅)₂MoH₂.² In addition, a modified synthetic method for (η^5 -C₅Me₅)₂MoH₂ was reported to proceed with insufficient yield for it to be useful as a starting material for subsequent derivatization.³ More recently, reproducible syntheses of (η^5 -C₅Me₅)₂MoCl₂, (η^5 -C₅Me₅)₂MoH₂, and a variety of other derivatives have been reported.⁴⁻⁶ Of these, synthetic details for (η^5 -C₅Me₅)₂MoCl₂ and (η^5 -C₅Me₅)₂MoH₂ are described here.

(η^5 -C₅Me₅)₂MoCl₂ is obtained by a two-step sequence involving (i) the reaction of MoCl₅ with a mixture of KC₅Me₅ and NaBH₄ to give crude (η^5 -C₅Me₅)₂MoH₂, followed by (ii) addition of CHCl₃. The latter step is important because the lower solubility of (η^5 -C₅Me₅)₂MoCl₂ in pentane compared to that of (η^5 -C₅Me₅)₂MoH₂ facilitates isolation of the organomolybdenum products. Specifically, the greater solubility of (η^5 -C₅Me₅)₂MoH₂ makes it difficult to separate the complex from oily by-products such as C₅Me₅H and (C₅Me₅)₂.

(η^5 -C₅Me₅)₂MoCl₂ is a useful precursor for a variety of other permethylmolybdenocene derivatives, which include hydride, alkyl, carbonyl, and oxo complexes, as illustrated in Scheme 1.⁴ For example, the dihydride (η^5 -C₅Me₅)₂MoH₂ is readily obtained by reaction of (η^5 -C₅Me₅)₂MoCl₂ with LiAlH₄.

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Scheme 1.

General Procedures

All manipulations are performed using a combination of inert atmosphere glove box and Schlenk techniques. Solvents are purified and degassed by standard procedures. All commercially available reagents are used as received without any further purification. Potassium pentamethylcyclopentadienide (KC_5Me_5) is synthesized by a literature route.⁷ ^1H and ^{13}C NMR chemical shifts are reported in ppm relative to SiMe_4 (δ 0) and are referenced internally to the residual ^1H NMR resonance (δ 7.15 for $\text{C}_6\text{D}_5\text{H}$) or ^{13}C NMR resonance (δ 128.0 for C_6D_6) of the solvent.

A. BIS(PENTAMETHYLCYCLOPENTADIENYL)-DICHLOROMOLYBDENUM(IV)

Procedure

■ **Caution.** *Tetrahydrofuran (THF) is flammable and forms explosive peroxides upon prolonged exposure to air. Sodium borohydride (NaBH_4) reacts violently with acids and acidic solutions to form hydrogen, which can form explosive mixtures with air. Chloroform is a suspected carcinogen.*

A sample of MoCl_5 (4.02 g, 14.7 mmol) is placed in a Schlenk tube (see, for example, Chemglass AF-0538-23), cooled to -78°C , and treated sequentially with toluene (10 mL) and THF (50 mL) that had been precooled to -78°C . The dark suspension is then added through a wide-bore cannula to a mixture of KC_5Me_5 (15.70 g, 90.06 mmol), NaBH_4 (1.49 g, 39.4 mmol), and THF (150 mL) in a 350 mL glass vessel (see, for example, Chemglass AF-0096-04) equipped with a Teflon stopcock at -78°C . The resulting mixture is allowed to warm to room temperature and stirred for 3 h. After this period, the mixture is heated for 24 h at 65°C . The volatile components are removed from the mixture and the residue is dried in vacuum overnight. The residue is extracted into pentane (200 mL) and filtered. The filtrate is concentrated to 100 mL and treated with CHCl_3 (5 mL). The mixture is stirred overnight at room temperature and the resulting precipitate is isolated by filtration, washed with pentane (2×30 mL), and dried in vacuum to give $(\eta^5\text{-C}_5\text{Me}_5)_2\text{MoCl}_2$ as a brown solid. Yield: 4.13 g (64%).*

Anal. Calcd. for $\text{C}_{20}\text{H}_{30}\text{Cl}_2\text{Mo}$: C, 54.9; H, 6.9. Found: C, 54.3; H, 7.2.

Properties

The IR spectrum of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{MoCl}_2$ as a KBr disk shows peaks at 2959 (s), 2904 (vs), 1456 (vs), 1374 (vs), 1069 (m), 1019 (vs), 804 (w), 679 (w), 609 (w), and 415 (w) cm^{-1} . Its ^1H NMR spectrum in C_6D_6 contains a singlet at δ 1.46, and its ^{13}C NMR spectrum in C_6D_6 shows resonances at δ 11.3 (q, $^1J_{\text{C-H}} = 128$, C_5Me_5) and 108.9 (s, C_5Me_5).

*The checkers obtained yields of 55–61%. They also emphasize the need for using a wide-bore cannula to avoid losses during transfer of the MoCl_5 /THF suspension, which tends to clump.

B. BIS(PENTAMETHYLCYCLOPENTADIENYL)-DIHYDRIDOMOLYBDENUM(IV)

Procedure

■ **Caution.** Diethyl ether is flammable. Lithium aluminum hydride (LiAlH_4) reacts violently with water, acids, and acidic solutions, and can decompose violently upon heating to produce hydrogen gas, which can form explosive mixtures with air.

To a stirred suspension of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{MoCl}_2$ (1.00 g, 2.29 mmol) in Et_2O (30 mL) is added LiAlH_4 (14 mL of a 1.0 M solution in Et_2O , 14 mmol) at -78°C . The mixture is allowed to warm slowly to room temperature and stirred overnight. After this period, the mixture is cooled to 0°C and treated dropwise with degassed water (2 mL). The mixture is allowed to warm to room temperature and stirred for 1 h. The volatile components are removed in vacuum, the residue is extracted into pentane (~ 100 mL), and the mixture is filtered. The filtrate is concentrated to ~ 2 mL and cooled to -78°C for ~ 1 h, thereby depositing $(\eta^5\text{-C}_5\text{Me}_5)_2\text{MoH}_2$ as a green-brown solid that is isolated by filtration and dried in vacuum. Yield: 0.52 g (62%).*

Anal. Calcd. for $\text{C}_{20}\text{H}_{32}\text{Mo}$: C, 65.2; H, 8.8. Found: C, 65.3; H, 9.2.

Properties

The IR spectrum of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{MoH}_2$ as a KBr disk shows bands at 2975 (vs), 2898 (vs), 2712 (m), 1864 (s, $\nu_{\text{Mo-H}}$), 1478 (s), 1452 (s), 1426 (s), 1375 (vs), 1069 (m), 1028 (vs), 908 (w), 884 (w), 792 (w), 670 (w), 590 (w), and 414 (w) cm^{-1} . Its ^1H NMR spectrum in C_6D_6 features resonances at $\delta -8.35$ (s, MoH_2) and 1.85

*The checkers obtained a yield of 46–57% in the first crop, but were able to isolate an additional 20% by concentrating and cooling the mother liquors. They also report that, although the green-brown product is analytically and spectroscopically pure, the dihydride can be sublimed at 100°C and 10^{-3} mmHg with minimal loss to afford a yellow solid, which they propose is the true color of this compound.

(s, C₅Me₅), and its ¹³C NMR in C₆D₆ exhibits peaks at δ 12.2 (q, ¹J_{C-H} = 126, C₅Me₅) and 92.9 (s, C₅Me₅).

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References

1. J. L. Thomas, *J. Am. Chem. Soc.* **95**, 1838 (1973).
2. F. G. N. Cloke, J. P. Day, J. C. Green, C. P. Morley, and A. C. Swain, *J. Chem. Soc., Dalton Trans.* 789 (1991).
3. T. Ito and T. Yoden, *Bull. Chem. Soc. Jpn.* **66**, 2365 (1993).
4. J. H. Shin, D. G. Churchill, B. M. Bridgewater, K. L. Pang, and G. Parkin, *Inorg. Chim. Acta* **359**, 2942 (2006).
5. J. H. Shin, B. M. Bridgewater, D. G. Churchill, M.-H. Baik, R. A. Friesner, and G. Parkin, *J. Am. Chem. Soc.* **123**, 10111 (2001).
6. K. E. Janak, J. H. Shin, and G. Parkin, *J. Am. Chem. Soc.* **126**, 13054 (2004).
7. V. C. Gibson, J. E. Bercaw, W. J. Bruton Jr., and R. D. Sanner, *Organometallics* **5**, 976 (1986).

13. (η^5 -CYCLOPENTADIENYL)TRICARBONYLMANGANESE(I) COMPLEXES

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Since the initial preparation of (η^5 -C₅H₅)Mn(CO)₃ by Fischer and Jira in 1954,¹ many methods have been developed for the synthesis of this compound (often referred to as “cymantrene”) and its C₅ substituted derivatives.² Interestingly, each of these preparations has at least one significant drawback from a preparative perspective (e.g., thallium reagents, high pressures, poor yields, or reactants that require significant preparative investment).

Surprisingly missing from this collection of preparative methods is the direct reaction between commercially available Mn(CO)₅Br and NaC₅H₅. This omission suggests that the reaction proceeds in poor yields, which is consistent with our experience. In 1988, however, Smart and coworkers found MnBr(CO)₃(pyridine)₂³ to be an effective reagent in making a substituted

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