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Convenient Synthesis of $[Et_4N]_2[M_2(CO)_8(\mu\text{-}H)_2]$ ($M = Mo, W$)

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Summary: $[Et_4N]_2[W_2(CO)_8(\mu\text{-}H)_2]$ and $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}H)_2]$ were synthesized in 47 and 31% yields, respectively, from the reaction of (TMED)$M(CO)_4$ ($M = Mo, W$; TMED = N,N,N′,N′-tetramethylethylenediamine) with a stoichiometric quantity of $[Et_4N][BH_4]$.

Introduction

Transition-metal hydrides are important intermediates in numerous catalytic hydroformylation, hydrogenation, and hydrogenolysis reactions.[1] Complexes containing terminal or bridging hydrido ligands have also been reported to effectively reduce organic molecules such as aldehydes, ketones, and alkyl halides.[2] Additionally, interest in transition-metal hydrides stems from the fact that they provide good models for several fundamental industrial processes.[3] Among metal hydrides, those containing the unsaturated moiety $M_2(\mu\text{-}H)_2$ ($M{=}M$) are attractive because of the presence of readily available vacant sites for the incoming substrates. Several such complexes have been reported, including $Os_3(CO)_{10}(\mu\text{-}H)_2$,[4] $[Re(CO)_4]_2(\mu\text{-}H)_2$,[5] $[M(CO)_3]_2(\mu\text{-}H)_2(\mu\text{-}L)$ ($M = Mn$, Re; L = diphosphine),[6] $[(\eta^5\text{-}C_5Me_5)Os(CO)]_2(\mu\text{-}H)_2$,[7] $[CpW(NO)H]_2(\mu\text{-}H)_2$,[8] $Re_3(\mu\text{-}H)_4(CO)_{10}^-$,[9] and $[M_2(CO)_4]_2(\mu\text{-}H)_2^{2-}$ ($M = W$, Mo).[10] The reactivity of $Os_3(CO)_{10}(\mu\text{-}H)_2$ has been studied extensively in the past.[11] $[M(CO)_3]_2(\mu\text{-}H)_2(\mu\text{-}L)$ ($M = Mn$, Re)[12] and $Re_3(\mu\text{-}H)_4(CO)_{10}^-$,[13] have also been the subject of many reports. In comparison, the reactivity of $[M(CO)_4]_2(\mu\text{-}H)_2^{2-}$ ($M = W$, Mo) species remains unexplored.[10,14] Similar to $Os_3(CO)_{10}(\mu\text{-}H)_2$[11] and $[Re(CO)_4]_2(\mu\text{-}H)_2$,[15] the complexes $[M(CO)_4]_2(\mu\text{-}H)_2^{2-}$ ($M = W$, Mo) should be useful in the construction of metal clusters. Although the complexes $[M(CO)_4]_2(\mu\text{-}H)_2^{2-}$ ($M = W$, Mo) can be synthesized as Et_4N^+ salts in moderate yields, one has to deal with extremely air-sensitive compounds, $Na_4M(CO)_4$, and noxious ammonia gas.[10a] In this paper, we will describe a convenient synthesis of $[Et_4N]_2[M_2(CO)_8(\mu\text{-}H)_2]$ from (TMED)$M(CO)_4$. This method is simple, the yield is comparable to that of the previous method, and it will facilitate the investigation of these interesting complexes.

Results and Discussion

The complex $[Et_4N]_2[W_2(CO)_8(\mu\text{-}H)_2]$ was first synthesized in very low yield from $W(CO)_6$ and $[Et_4N][BH_4]$.[10b] Apparently, the necessity of evolution of two CO ligands per W atom renders the reaction difficult. Later, Kirtley reported the synthesis of $[PPN]_2[W_2(CO)_8(\mu\text{-}H)_2]$ from $[PPN][W(CO)_5I]$ with $[PPN][BH_4]$.[16] We found that the latter method was not appropriate for the synthesis of the molybdenum analogue, possibly

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(1) (a) Ojima, I.; Eguchi, M.; Tzamarioudaki, M. in *Comprehensive Organometallic Chemistry II*; Hegedus, L. S., Ed.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 9. (b) Collman, J. P.; Hegedus, L. S., Norton, J. R., Finke, R. G., Eds. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (c) Slocum, D. W., Moser, W. R., Eds. *Catalytic Transition Metal Hydrides*; New York Academy of Sciences: New York, 1983. (d) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

(2) (a) Chisholm, M. H.; Kramer, K. S. *Chem. Commun.* **1996**, 1331. (b) Ash, C. E.; Hurd, P. W.; Darensbourg, M. Y.; Newcomb, M. *J. Am. Chem. Soc.* **1987**, *109*, 3313. (c) Gaus, P. L.; Kao, S. C.; Youngdahl, K.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1985**, *107*, 2428. (d) Kao, S. C.; Spillett, C. T.; Ash, C.; Lusk, R.; Park, Y. K.; Darensbourg, M. Y. *Organometallics* **1985**, *4*, 83. (e) Kao, S. C.; Gaus, P. L.; Youngdahl, K.; Darensbourg, M. Y. *Oganometallics* **1984**, *3*, 1601. (f) Kao, S. C.; Darensbourg, M. Y. *Organometallics* **1984**, *3*, 656. (g) Boldrini, G. P.; Umani-Ronchi, A. *J. Organomet. Chem.* **1979**, *171*, 85. (h) Kinney, R. J.; Jones, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1978**, *100*, 7902. (i) Collman, J. P.; Finke, R. G.; Matlock, P. L.; Wahren, R.; Komoto, R. G.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 1119. (j) Boldrini, G. P.; Umani-Ronchi, A. *Synthesis* **1976**, 596.

(3) (a) Matsubara, K.; Okamura, R.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc.* **1998**, *120*, 1108. (b) Adams, R. D.; Barnard, T. S.; Li, Z.; Wu, W.; Yamamoto, J. H. *J. Am. Cham. Soc.* **1994**, *116*, 9103. (c) Miller, R. L.; Toreki, R.; LaPointe, R. E.; Wolczanski, P. T.; Van Duyne, G. D.; Roe, D. C. *J. Am. Chem. Soc.* **1993**, *115*, 5570. (d) Casey, C. P.; Widenhoefer, R. A.; Hallenbeck, S. L.; Gavney, J. A., Jr. *J. Chem. Soc., Chem. Commun.* **1993**, 1692.

(4) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* **1975**, *97*, 3942.

(5) Andrews, M. A.; Kirtley, S. W.; Kaesz, H. D. *Inorg. Chem.* **1977**, *16*, 1556.

(6) (a) Aspinall, H. C.; Deeming, A. J. *J. Chem. Soc., Chem. Commun.* **1983**, 838. (b) Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1505. (c) Mays, M. J.; Prest, D. W.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1980**, 171.

(7) Hoyano, J. K.; Graham, W. A. G. *J. Am. Chem. Soc.* **1982**, *104*, 3722.

(8) Legzdins, P.; Martin, J. T.; Einstein, F. W. B.; Willis, A. C. *J. Am. Chem. Soc.* **1986**, *108*, 7971.

(9) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Molinari, H.; Sironi, A. *Inorg. Chem.* **1985**, *24*, 2666.

(10) (a) Lin, J. T.; Hagen, G. P.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2296. (b) Churchill, M. R.; Chang, S. W. Y. *J. Chem. Soc., Chem. Commun.* **1973**, 691.

(11) (a) Deeming, A. J. *Adv. Organomet. Chem.* **1986**, *26*, 1. (b) Burgess, K. *Polyhedron* **1984**, *3*, 1176.

(12) (a) Alonso, F. J. G.; Sanz, M. G.; Liu, X. Y.; Oliveira, A.; Ruiz, M. A.; Riera, V.; Bois, C. *J. Organomet. Chem.* **1996**, *511*, 93 and references therein. (b) Garcia Alonso, F. J.; Garcia Sanz, M.; Riera, V.; Ruiz, M. A.; Tiripicchio, A.; Tiripicchio Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1167. (c) Prest, D. W.; Mays, M. J.; Raithby, P. R. *J. Chem. Soc., Dalton Trans.* **1982**, 2021. (d) Bruce, M. I.; Wallis, R. C. *J. Chem. Soc., Chem. Commun.* **1982**, 253.

(13) (a) Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Organometallics* **1997**, *16*, 2719. (b) Beringhelli, T.; Ciani, G,; D'Alfonso, G.; Freni, M. *J. Organomet. Chem.* **1986**, *311*, C51.

(14) (a) Lin, J. T.; Hsiao, Y. M.; Liu, L. K.; Yeh, S. K. *Organometallics* **1988**, *7*, 2065. (b) Lin, J. T.; Shiao, Y. M. *J. Organomet. Chem.* **1987**, *334*, C31.

(15) (a) Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Mercandelli, P.; Moret, M.; Sironi, A. *Organometallics* **1997**, *16*, 4129. (b) Bergamo, M.; Beringhelli, T.; D'Alfonso, G.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1996**, *15*, 3876. (c) Antognazza, P.; Beringhelli, T.; D'Alfonso, G.; Minoja, A.; Ciani, G.; Moret, M.; Sironi, A. *Organometallics* **1992**, *11*, 1777.

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because of the enhanced CO lability in molybdenum carbonyls, and the evolved CO rapidly destroyed any $Mo_2(CO)_8(\mu\text{-}H)_2^{2-}$ formed.[10a] Metal complexes with substitution-labile and chemically inert polydentate amine ligands can potentially create several vacant sites at the metal center for facile derivatization. Indeed, such a strategy has been successfully applied in the construction of highly reduced organometallic complexes,[10a] metal clusters[17,18] and simple ligand substitution.[19] By the same strategy we have been able to synthesize $[Et_4N]_2[M_2(CO)_8(\mu\text{-}H)_2]$ (M = Mo, W) from (TMED)$M(CO)_4$ (M = Mo, W; TMED = *N,N,N′,N′*-tetramethylethylenediamine) and $[Et_4N][BH_4]$ (eq 1).

$$(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)M(CO)_4 + [Et_4N][BH_4] \xrightarrow[70\ °C/THF\ (M = W)]{60\ °C/THF\ (M = Mo)} \quad (1)$$

A speculative mechanism for the formation of $W_2(CO)_8(\mu\text{-}H)_2^{2-}$ in the present method, involves a reversible ring opening (with scission at the M−N bond) followed by nucleophilic attack by H^-. Such a mechanism has been proposed in the reaction of $Mo(CO)_3(PNP)$ (PNP = $Ph_2PCH_2CH_2N(Et)CH_2CH_2PPh_2$) with CO.[20] It is interesting to note that the similar reaction of (TMED)$W(CO)_4$ with K[*sec*-Bu_3BH] also affords $K_2[H_2W(CO)_4]$.[10a] The reaction conditions are also important, especially for the synthesis of **3**. The deviation in temperature for the reaction can be no more than ca. ±3 °C; a lower temperature results in a lower yield, whereas a higher temperature leads to substantial formation of $[Mo(CO)_3(\mu_3\text{-}H)]_4$.[4−18] Another critical step in the reaction is the washing of the crude $[Et_4N]_2[M_2(CO)_8(\mu\text{-}H)_2]$ with water. The washing should be accomplished as rapidly as possible, particularly for **3**, to avoid decomposition of the desired product (vide infra). The most important accomplishment in this study is the convenient syntheses of $[Et_4N]_2[M_2(CO)_8(\mu\text{-}H)_2]$ (M = Mo, W) in yields comparable with that reported previously. A larger scale preparation should also be conceivable, in view of the simplicity of the reaction setup.

Although complex **3** in its solid form can be handled in air for several hours without apparent decomposition, in solution it reacts readily with H_2O to produce $[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)]_4$, along with $[Et_4N][Mo_2(CO)_{10}(\mu\text{-}H)]$. The latter compound is produced possibly by protonation of $Mo_2(CO)_{10}^{2-}$, formed in situ from the reaction of the released CO with unreacted **3**.[16] The complex **2** dissolved in CH_3CN also reacts with H_2O at a slower rate. The major product obtained from the reaction is $[Et_4N][W_2(CO)_{10}(\mu\text{-}H)]$.[21] Our preliminary study indicates that interesting heteronuclear metal clusters such as $W_2(CO)_8(\mu\text{-dppm})(\mu\text{-}H)(\mu\text{-}CuPPh_3)$ can be derived from $[Et_4N]_2[W_2(CO)_8(\mu\text{-}H)_2]$.[22] The synthetic exploitation of **2** and **3** to assemble metal clusters will be pursued in a future study.

Experimental Section

General Procedure. Infrared measurements were made on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer. The ^1H NMR spectra were recorded on a Bruker AC300 spectrometer and referenced to TMS. Elemental analyses were performed on a Perkin-Elmer 2400 CHN analyzer.

Unless specified, all operations were carried out under nitrogen with use of standard Schlenk techniques or a drybox. All solvents were purified by standard procedures or degassed by bubbling nitrogen through the solvents for 1 h prior to use. (TMED)$M(CO)_4$ (M = Mo, W; TMED = *N,N,N′,N′*-tetramethylethylenediamine) were prepared according to the published procedures.[23]

Synthesis of $[Et_4N][BH_4]$ (1). Anhydrous CH_3CN (1000 mL) was added to a flask containing a mixture of $Et_4N^+Br^-$ (45.0 g, 0.214 mol) and $NaBH_4$ (8.10 g, 0.214 mol), the resulting slurry was stirred at room temperature for 48 h, and the solution was filtered. The filtrate was pumped dry, and the residue was washed with Et_2O to provide white crystalline **1** in 97% yield (30.1 g). Anal. Calcd for $BC_8H_{24}N$: C, 66.22; H, 16.67; N, 9.65. Found: C, 66.41, H, 16.49; N, 9.33.

Synthesis of $[Et_4N]_2[W_2(CO)_8(\mu\text{-}H)_2]$ (2). To a flask containing (TMED)$W(CO)_4$ (10.0 g, 24.2 mmol) and $[NEt_4][BH_4]$ (4.05 g, 27.9 mmol) was added 150 mL of THF, and the resulting slurry was heated to 72 °C for 48 h. During the reaction a reddish precipitate formed at the expense of white $[NEt_4][BH_4]$. THF was removed from the red solid via a cannula. The red solid was then washed with H_2O (100 mL × 3) in air and pumped dry. Recrystallization of the red powder from acetone and THF provided red crystalline **2** in 47% yield (4.85 g). Anal. Calcd for $C_{24}H_{42}N_2O_8W_2$: C, 33.74; H, 4.96; N, 3.28. Found: C, 33.42, H, 4.92; N, 3.39.

Synthesis of $[Et_4N]_2[Mo_2(CO)_8(\mu\text{-}H)_2]$ (3). To a flask containing (TMED)$W(CO)_4$ (5.0 g, 15.3 mmol) and $[NEt_4][BH_4]$ (2.69 g, 18.5 mmol) was added 150 mL of THF, and the resulting slurry was heated at 58−60 °C for 15 h. During the reaction the white $[NEt_4][BH_4]$ gradually disappeared and an orange precipitate formed. The supernatant was removed using a cannula, and the remaining red powder was recrystallized from acetone (300 mL × 5) under a nitrogen atmosphere. The resulting orange solid was then washed with THF (100 mL × 3), H_2O (100 mL × 3), and THF (100 mL × 2) in air and pumped dry. Further recrystallization of the red powder from CH_3CN and THF afforded orange crystalline **2** in 31% yield (1.6 g). Anal. Calcd for $C_{24}H_{42}N_2O_8Mo_2$: C, 42.49; H, 6.24; N, 4.13. Found: C, 42.40, H, 6.16; N, 4.22.

Reaction of 3 with H_2O. Degassed H_2O (2.0 mL) was added to a solution of **3** (300 mg, 0.442 mmol) in 30 mL of CH_3CN. After the solution was stirred for 24 h at room temperature, the solvent was removed in vacuo. The residue was washed with THF (10 mL × 2) and CH_3CN (2 mL × 2) and pumped dry to provide 130 mg of yellow powdery $[Et_4N]_4[Mo(CO)_3(\mu_3\text{-}OH)]_4$ (45%).[17] From the THF washings the complex $[Et_4N][Mo_2(CO)_{10}(\mu\text{-}H)]$[21] was isolated in 52% yield (140 mg).

Reaction of 2 with H_2O. H_2O (2.0 mL) was added to a solution of **2** (150 mg, 0.176 mmol) in 30 mL of CH_3CN. The solution was stirred for 48 h at room temperature and concentrated to ca. 1 mL. The supernatant was discarded and the residue was pumped dry. The residue was then recrystallized from THF/Et_2O to afford yellow powdery $[Et_4N][W_2(CO)_{10}(\mu\text{-}H)]$[21] in 86% yield (120 mg).

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(16) Wei, C. Y.; Bau, R.; Kirtley, S. W.; Bisson, D. E. *Inorg. Chem.* **1982**, *21*, 2556.

(17) Lin, J. T.; Yeh, S. K.; Lee, G. H.; Wang, Y. *J. Organomet. Chem.* **1989**, *361*, 89.

(18) Lin, J. T.; Ellis, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 6252.

(19) Zanotti, V.; Rutar, V.; Angelici, R. J. *J. Organomet. Chem.* **1991**, *414*, 177.

(20) Knebel, W. J.; Angelici, R. J. *Inorg. Chem.* **1974**, *13*, 632.

(21) Hayter, R. G. *J. Am. Chem. Soc.* **1966**, *88*, 4376.

(22) Lin, J. T.; Yu, C. C.; Huang, P. S., unpublished research.

(23) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.