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LETTER

Synthetic Applications of the Oxidative Cleavage of the Molybdenum–Mercury Bonds in $[CpMo(CO)_2(PPh_3)]_2Hg$

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It has long been known that oxidation or reduction can cleave metal–metal bonds in transition metal organometallics [1]. In particular, dimers of cyclopentadienyliron [2–5] and cyclopentadienylmolybdenum [6] species can be either oxidatively or reductively cleaved to yield fragments which are synthetically useful. Oxidative cleavages are usually accompanied by coordination of solvent or other ligand to the cationic products. Products with weakly bound anions or solvent are useful for the synthesis of substituted complexes [7].

We wish to report here the syntheses of complexes of the type $CpMo(CO)_2(PPh_3)L^{+/0}$ (L = nitrile, phosphine or halide) through the oxidative cleavage of the molybdenum–mercury bonds in the linear trimetallic complex $[CpMo(CO)_2(PPh_3)]_2Hg$ ($Cp = \eta^5\text{-}C_5H_5$) (**1**). The oxidative cleavage presumably generates the previously reported tetrafluoroborate complex $CpMo(CO)_2(PPh_3)FBF_3$ (**2**) [8], which reacts *in situ* with neutral or anionic ligands to give good yields of the substituted complexes. However, whereas the previously reported synthesis of **2** involved hydride abstraction from the extremely air-sensitive $CpMo(CO)_2(PPh_3)H$ and required temperatures of −40 to −55 °C, our syntheses begin with the reasonably air-stable compound **1** and are carried out at room temperature.

Experimental

The complexes $[CpMo(CO)_2(PPh_3)]_2Hg$ (**1**) [9] and ferrocenium tetrafluoroborate, $FcBF_4$, [10] were prepared according to the literature procedures. Solvents were distilled under nitrogen before use: dichloromethane (Fisher Optima) from calcium hydride; acetonitrile (Burdick and Jackson, distilled in glass) from phosphorus pentoxide; and tetrahydrofuran (Fisher Optima) from Na/benzophenone. All other chemicals were reagent grade or better.

IR spectra were obtained using a Mattson Instruments Cygnus 100 FT-IR and ^{1}H NMR spectra were obtained on a JEOL FX-90Q spectrometer. The elemental analysis was performed by Galbraith Laboratories, Knoxville, TN, U.S.A.

cis-$[CpMo(CO)_2(PPh_3)(CH_3CN)]^+BF_4^-$ (3)

To a solution of **1** (0.500 g, 0.431 mmol) in 3:1 vol./vol. CH_2Cl_2/CH_3CN (15 ml) under nitrogen was added $FcBF_4$ (0.235 g, 0.861 mmol). After stirring for 1 h at room temperature, the solution was filtered to remove metallic mercury and the solvent was removed on a rotary evaporator. The residue was redissolved in 10 ml of CH_2Cl_2 and then 25 ml of CCl_4 was slowly added to precipitate *cis*-$[CpMo(CO)_2(PPh_3)(CH_3CN)]^+BF_4^-$ (**3**) (yield, 0.439 g; 84%). Analytically pure single crystals were prepared by layering toluene over a solution of **3** in dichloromethane. IR (CH_2Cl_2): 1992vs, 1920s cm^{-1}. ^{1}H NMR (CD_2Cl_2): δ 7.4(m), 5.63(s), 1.83 (d, $J_{PH} = 2.5$ Hz). *Anal.* Calc. for $C_{27}H_{23}BF_4MoNO_2P$: C, 53.41; H, 3.82; N, 2.31. Found: C, 53.82; H, 3.87; N, 2.24.

trans-$[CpMo(CO)_2(PPh_3)_2]^+BF_4^-$

To a solution of **1** (0.500 g, 0.431 mmol) in CH_2Cl_2 (50 ml) under argon was added $FcBF_4$ (0.235 g, 0.861 mmol). After stirring the solution for 2 h at room temperature, PPh_3 (0.226 g, 0.861 mmol) was added. After stirring for an additional 15 min, the solution was filtered and the solvent was removed on a rotary evaporator. The residue was redissolved in 5 ml of CH_2Cl_2 and then 50 ml of diethyl ether was slowly added to precipitate *trans*-$[CpMo(CO)_2(PPh_3)_2]^+BF_4^-$, which was recrystallized from CH_2Cl_2/isopropanol (yield, 0.346 g; 48%). IR (CH_2Cl_2): 1977s, 1900vs cm^{-1} (1978s, 1901vs [8]). ^{1}H NMR (CD_2Cl_2): δ 7.5(m), 5.06 (t, $J_{PH} = 1.2$ Hz) (5.03(t) [8]).

$CpMo(CO)_2(PPh_3)I$

A solution of **1** was oxidized as in the previous preparation and, after stirring for 2 h, tetrabutylammonium iodide (0.318 g, 0.861 mmol) was added. After stirring for an additional 15 min the solvent was removed. The residue was dissolved in $CHCl_3$ and chromatographed on florisil. After chro-

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matography the $CHCl_3$ was removed and the product was recrystallized from CH_2Cl_2/heptane (yield, 0.399 g; 76%). IR ($CHCl_3$): 1969vs, 1885s cm^{-1} (1975, 1890 [11]). ^1H NMR ($CDCl_3$): δ 7.4(m), 5.35 (s, *cis*), 5.08 (d, J_{PH} = 1.8 Hz, *trans*) (*cis* 5.35(s), *trans* 5.07 (d, J_{PH} = 1.5 Hz) [11]).

Results and Discussion

Ferrocenium tetrafluoroborate, $FcBF_4$, oxidizes **1** in CH_2Cl_2, resulting in an immediate change in the color of the solution from yellow to reddish brown. IR spectra show that the addition of two equivalents of $FcBF_4$ causes the carbonyl stretching bands of **1** at 1972, 1890, 1863 and 1815 cm^{-1} to be replaced by new ones at 1988, 1906 and 1856 cm^{-1}. With time, the 1988 and 1906 cm^{-1} bands increase as the 1856 cm^{-1} band decreases. During this time metallic mercury is seen to precipitate. After 1 to 2 h the 1856 cm^{-1} band reaches a small constant intensity. The remaining intense carbonyl stretching bands have frequencies similar to those reported for $CpMo(CO)_2(PPh_3)FBF_3$ [8], which is the most likely product of the oxidation in the absence of a coordinating solvent or other potential ligand.

Stable complexes of the type $CpMo(CO)_2(PPh_3)L^{+/0}$ can be prepared by addition of the ligand L to solutions of **2** in CH_2Cl_2 [8]. We have prepared several such derivatives. An example of the synthesis of a cationic derivative is *trans*-$[CpMo(CO)_2(PPh_3)_2]^+BF_4^-$, prepared by oxidative cleavage of **1** to **2** in CH_2Cl_2, followed by addition of one equivalent of PPh_3. Anionic ligands can also be introduced through our route. Oxidation of **1** followed by addition of tetrabutylammonium iodide resulted in formation of $CpMo(CO)_2(PPh_3)I$. In this case NMR spectroscopy indicated an approximately 40:1 *cis*/*trans* isomer ratio.

The time between the additions of $FcBF_4$ and the substituting ligand is important. The initial reaction between **1** and ferrocenium is fast, but apparently a slow chemical reaction follows. We believe the cleavage of the first Mo–Hg bond is rapid but the cleavage of the second Mo–Hg bond is much slower. Thus, time must be allowed for this slow cleavage to proceed before the ligand is added. However, since the tetrafluoroborate complex is not thermally stable [8], reaction times which are too long give significant amounts of impurities which are very difficult to remove. We find that waiting 1 to 2 h after oxidation gives time for nearly complete cleavage of both Mo–Hg bonds but avoids extensive decomposition of the tetrafluoroborate complex. Nevertheless, 1 or 2% of Cp-containing impurities are generally found in the isolated products.

A previously unreported derivative we have prepared is *cis*-$[CpMo(CO)_2(PPh_3)(CH_3CN)]^+BF_4^-$ (**3**). This compound is best prepared by oxidation of **1** with two equivalents of $FcBF_4$ in a 3:1 mixture of CH_2Cl_2/CH_3CN, although it can also be prepared by oxidation of **1** in pure CH_2Cl_2 followed by addition of CH_3CN. The identity of **3** has been confirmed by an X-ray crystal structure [12] and its geometry established to be *cis*, in agreement with the greater intensity of the high frequency (symmetric) carbonyl stretch in the IR and the singlet observed in the ^1H NMR for the cyclopentadienyl protons [11].

Thus, we have shown that both cationic and neutral complexes of the type $CpMo(CO)_2(PPh_3)L^{+/0}$ can be prepared from the stable and easily synthesized starting material $[CpMo(CO)_2(PPh_3)]_2Hg$. Ligands other than those reported should react similarly, and other complexes of the type $[CpMo(CO)_{3-n}L_n]_2Hg$ should be viable starting materials, although perhaps requiring different oxidants. Yields are somewhat lower than those obtained by other routes because of thermal decomposition of the tetrafluoroborate complex and necessary purification, but we feel that the ease of synthesis of both the starting material and the substituted complexes more than makes up for some loss in yield.

In addition to providing a new synthetic route to complexes of the type $CpMo(CO)_2(PPh_3)L^{+/0}$, we have found unusual mechanistic features in the oxidative cleavage of **1**. The consumption of only two equivalents of oxidant with the generation of metallic mercury was quite unexpected. We had expected the reaction to consume four equivalents of oxidant and produce **2** and Hg^{2+}. In addition, we can observe by IR spectroscopy an intermediate in the cleavage with a CO stretching frequency of 1856 cm^{-1}. We are currently investigating the mechanism of the oxidative cleavage of **1** and will report on it in due course.

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