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Single-Flask Synthesis of $(C_5H_5)W(CO)_3Cl$ from $W(CO)_6$

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$(C_5H_5)W(CO)_3Cl$ has been prepared in >90% yield from $W(CO)_6$, cyclopentadiene, and CCl_4 in a single-flask synthesis involving the intermediates $W(CO)_3(CH_3CN)_3$ and $(C_5H_5)W(CO)_3H$.

Introduction

Cyclopentadienylmolybdenumtricarbonyl halides can be relatively simply prepared by stoichiometric oxidation of the readily accessible metal–metal bonded dimer *1* (Cp = cyclopentadienyl) with elemental halogen (eqn. 1) [1, 2]. The analogous tungsten halide complexes have been less easily prepared using commonly available starting materials, since the tungsten analog of the molybdenum dimer *1* is not readily made from $W(CO)_6$ and cyclopentadiene or the cyclopentadienyl anion [3]. As a result, fewer reactions of the cyclopentadienyltungsten halides have been reported. We report herein a high-yield single-flask synthesis of $CpW(CO)_3Cl$ from $W(CO)_6$ and cyclopentadiene involving the known $W(CO)_3(CH_3CN)_3$ and $CpW(CO)_3H$ as intermediates.

$$\underset{1}{[CpMo(CO)_3]_2} + X_2 = 2CpMo(CO)_3X \quad X = I, Br, Cl \qquad (1)$$

$W(CO)_6$ was shown by Tate *et al.* [4] to be slowly converted in boiling CH_3CN to $W(CO)_3(CH_3CN)_3$. The latter compound when treated with cyclopentadiene afforded $CpW(CO)_3H$ in moderately good yields after purification by sublimation [5, 6]. That hydride could in turn be converted into $CpW(CO)_3Cl$ in nearly quantitative yield by CCl_4 [7]. We have now shown that not only can $W(CO)_3(CH_3CN)_3$ be transformed in high yield in a single vessel to $CpW(CO)_3Cl$ but that a single-flask synthesis starting with $W(CO)_6$ also proceeds smoothly.

Experimental

All compounds were handled under argon unless otherwise described. $W(CO)_6$ was used as purchased from Strem Chemicals. CH_3CN (reagent, J. T. Baker) was stored over Mol Sieve 4A and degassed before use. Tetrahydrofuran (THF) was freshly distilled under argon from sodium/benzophenone. Cyclopentadiene was used shortly after its preparation under argon via thermal cracking of technical grade dicyclopentadiene (Aldrich). CCl_4 (Aldrich) was used as received. $CHCl_3$ (MCB reagent) was passed through silica gel (10 ml through 2 cm diameter by 15 cm height column) to remove the ethanol preservative to preclude any effect due to presence of alcohol. $W(CO)_3(CH_3CN)_3$ was prepared after the manner of Keppie and Lappert [6]. A mixture of $W(CO)_6$ (7.0 g) and CH_3CN (75 ml) was heated at reflux for 7 days. The resulting bright yellow solution was cooled and stored at 0 °C for 36 h to afford bright yellow crystals; these were filtered, washed with cold CH_3CN, and dried by oil-pump vacuum (20 μ) at 20 °C for 1 h.

Preparation of $CpW(CO)_3Cl$ from $W(CO)_3(CH_3CN)_3$

A mixture of $W(CO)_3(CH_3CN)_3$ (4.45 g, 11.4 mmol), cyclopentadiene (10 ml), $CHCl_3$ (5.0 ml), and THF (50 ml) in a Schlenk tube fitted with magnetic stir-bar and reflux condenser was heated with a water bath from ambient to 50 °C. The initially yellow slurry became a moderately dark orange solution in 0.4 h. Stirring at 50 ± 3 °C was continued a total of 3 h. Then the bath was removed and CCl_4 (6 ml) was added to the warm orange-brown solution. The resulting solution darkened over several minutes to blood-red. It was allowed to cool to ambient and stir 4 h [8]. The clear, dark-red solution was concentrated by pump vacuum to afford dark red-orange crystals. Degassed heptane (20 ml; Aldrich) was added to ensure more complete precipitation; the resulting solid was filtered in air and washed with hexanes to afford 3.52 g of red-orange crystals. Stripping the combined filtrate and washings (aerobic procedure) gave a red oil; the latter was taken up in a small amount of CH_2Cl_2 and passed through a short, thick silica gel column to afford a red solution. Upon its concentration, a second crop of red-orange crystals was formed (0.44 g). The identity of the material as $CpW(CO)_3Cl$ was confirmed [9] by its infrared (ν(CO) in $CHCl_3$ 2053(s) and 1968(vs, broad) cm^{-1}) and proton nmr (singlet

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at 5.75 δ in $CDCl_3$) spectra. That the solids were not solvates was shown by ^1H nmr (no signal with intensity greater than 2% that of the Cp resonance observed) and GLC (no peak with retention time consistent with the presence of CCl_4 seen when a concentrated solution of the solids in CH_2Cl_2 injected). The combined yield of 3.96 g corresponded to 94.5% conversion of $W(CO)_3(CH_3CN)_3$ into $CpW(CO)_3Cl$.

Preparation of $CpW(CO)_3Cl$ *from* $W(CO)_6$

A mixture of $W(CO)_6$ (7.02 g, 20.0 mmol) and CH_3CN (75 ml) in a 250 ml Schlenk flask fitted with Friedrich condenser and magnetic stir-bar was heated at reflux 7 days. The resulting yellow solution was cooled to ambient temperature and stripped by oil-pump vacuum to a bright-yellow solid containing a small amount of gray-green impurity. The resulting material was treated in THF (90 ml) with cyclopentadiene (20 ml) and $CHCl_3$ (10 ml) followed by CCl_4 (12 ml) in a manner essentially identical to that described in the immediately preceeding preparation (same times). A similar work-up afforded two crops of red-orange crystals (combined yield of 6.65 g or 90.3%) with the appropriate ^1H nmr spectrum and infrared carbonyl stretching pattern.

Results and Discussion

$W(CO)_6$ has been converted into $CpW(CO)_3Cl$ in a high-yield (>90%) single-flask synthesis employing simple anaerobic apparatus and an uncomplicated procedure. The preparation apparently involves combination of three known reactions (eqns. 2–4) [4–7].

$$W(CO)_6 + 3CH_3CN = W(CO)_3(CH_3CN)_3 + 3CO \qquad (2)$$

$$W(CO)_3(CH_3CN)_3 + CpH = CpW(CO)_3H + 3CH_3CN \qquad (3)$$

$$CpW(CO)_3H + CCl_4 = CpW(CO)_3Cl + CHCl_3 \qquad (4)$$

Based on reports by Keppie and Lappert [6] of low yields of $CpW(CO)_3H$ for reaction 3 in CH_3CN solvent [10], we opted for running that portion of the synthesis in THF, even though it required stripping off the initial solvent and introducing another. $CHCl_3$ was added as a potential chlorine donor since it was unlikely to react with $W(CO)_3(CH_3CN)_3$ but might react with the hydride $CpW(CO)_3H$. Visual evidence (orange solution consistent with the presence of $CpW(CO)_3H$ [6] maintained for 3 h at 50 °C with $CHCl_3$ present but lost within minutes when CCl_4 added) suggests that little if any chlorination was due to $CHCl_3$ [11]. CCl_4 was not added until $W(CO)_3(CH_3CN)_3$ had apparently been completely converted into the hydride for fear of oxidizing the reactive zerovalent tris-acetonitrile complex.

Kubas [12] has recently reported that higher homologs of CH_3CN are superior to CH_3CN in convenience of preparation of $W(CO)_3(RCN)_3$ from $W(CO)_6$ and in reactivity (solubility and ease of displacement of coordinated nitrile by incoming ligand). Our single-flask synthesis of $CpW(CO)_3Cl$ should be even simpler using propionitrile or butyronitrile. If the steric bulk of $CH_3CH_2CH_2CN$ [13] (PrCN) makes it a sufficiently poor ligand, then it might be possible to prepare $CpW(CO)_3H$ from the crude reaction product mixture of $W(CO)_6$ plus excess PrPN (solvent) directly without removal of nitrile solvent; *i.e.*, in PrPN solvent the equilibrium of eqn. 3 might lie sufficiently far to the right to produce acceptable yields of $CpW(CO)_3Cl$ upon addition of CCl_4.

The single-flask synthetic technique successful for $CpW(CO)_3Cl$ should be extendable to its halide analogs (instead of CCl_4 as the halogenating agent for $CpW(CO)_3H$, $CHBr_3$, CBr_4, or N-bromosuccinimide to afford the bromide and CH_2I_2 or CHI_3 to give the iodide) and the nitrosyl $CpW(NO)(CO)_2$ (instead of CCl_4, the nitrosylating agent Diazald®, p-$CH_3C_6H_4SO_2N(CH_3)NO$ [14]). The technique [15] might also be extended to preparation of the chromium and molybdenum analogs of the halides and nitrosyls, for $CpCr(CO)_3H$ and $CpMo(CO)_3H$ have been prepared from the respective hexacarbonyls via tris-acetonitrile intermediates [6].

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References

1 $[CpMo(CO)_3]_2$ is a moderately-priced chemical (air-inert as solid and in solution in the dark) available from several vendors of organometallic compounds. It can be prepared from inexpensive $Mo(CO)_6$ and cyclopentadiene in good yield: R. B. King and F. G. A. Stone, *Inorg. Syntheses*, *7*, 99 (1963).
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7 (a) E. O. Fischer and K. Fichtel, *Chem. Ber., 94,* 1200 (1961).
(b) T. S. Piper and G. Wilkinson, *J. Inorg. Nucl. Chem., 3,* 104 (1956).

8 The air-inertness of $CpW(CO)_3Cl$ allows aerobic handling of the material from this point, even though this particular procedure maintained inert-atmosphere conditions through isolation of the first crop of crystals.

9 T. E. Sloan and A. Wojcicki, *Inorg. Chem., 7,* 1268 (1968).

10 $CpMo(CO)_3H$ is converted in CH_3CN solution at 25 °C to $Mo(CO)_3(CH_3CN)_3$ and CpH, the reverse of eqn. 3. R. F. Jordan and J. R. Norton, *J. Am. Chem. Soc., 104,* 1255 (1982). A similar phenomenon would explain the low yield of $CpW(CO)_3H$ from $W(CO)_3(CH_3CN)_3$ and excess CpH in CH_3CN in ref. 6.

11 $CHCl_3$ did appear to improve solubility, a factor of unknown importance in the synthesis.

12 G. J. Kubas, *Inorg. Chem., 22,* 692 (1983).

13 Kubas (ref. 12) reported that isobutyronitrile reacted much slower with $W(CO)_6$ than did its linear analog but provided no information as to whether $W(CO)_3(i\text{-}PrCN)_3$ could be prepared in good yield with extended heating. If so, the sec-alkyl nitrile should be bulkier than its n-alkyl analog and thus an even better prospect for single-solvent conversion of $W(CO)_6$ to $CpW(CO)_3Cl$.

14 ® Trademark of Aldrich Chemical Co., Inc. The reaction of transition-metal hydrides with Diazald to generate metal nitrosyls appears quite general, as illustrated in formation of $CpMo(CO)_2(NO)$ (ref. 7b) and $Rh(NO)(PPh_3)_3$ and $Ru(NO)_2(PPh_3)_2$ (J. J. Levison and S. D. Robinson, *Chem. Ind.,* 1514 (1969).

15 Single-flask conversions of $Ru_3(CO)_{12}$ with CpH into $CpRu(CO)_2X$ (X = Cl, Br) (A. Eisenstadt, R. Tannenbaum and A. Efraty, *J. Organometal. Chem., 221,* 317 (1981)) and $CpRu(CO)(PPh_3)Cl$ (A. F. Humphries and S. A. R. Knox, *J. Chem. Soc. Dalton,* 1710 (1975)) have been reported.