

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

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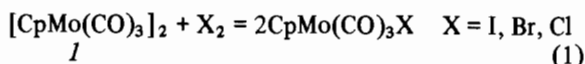
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$(C_5H_5)W(CO)_3Cl$  has been prepared in >90% yield from  $W(CO)_6$ , cyclopentadiene, and  $CCl_4$  in a single-flask synthesis involving the intermediates  $W(CO)_3(CH_3CN)_3$  and  $(C_5H_5)W(CO)_3H$ .

## Introduction

Cyclopentadienylmolybdenumtricarbonyl halides can be relatively simply prepared by stoichiometric oxidation of the readily accessible metal–metal bonded dimer  $I$  (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  $I$  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.

$W(CO)_6$  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  $\mu$ ) 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  $50 \pm 3$  °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 ( $\nu(CO)$  in  $CHCl_3$  2053(s) and 1968(vs, broad)  $cm^{-1}$ ) and proton nmr (singlet

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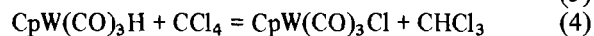
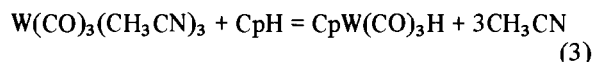
at 5.75  $\delta$  in  $\text{CDCl}_3$ ) spectra. That the solids were not solvates was shown by  $^1\text{H}$  nmr (no signal with intensity greater than 2% that of the Cp resonance observed) and GLC (no peak with retention time consistent with the presence of  $\text{CCl}_4$  seen when a concentrated solution of the solids in  $\text{CH}_2\text{Cl}_2$  injected). The combined yield of 3.96 g corresponded to 94.5% conversion of  $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$  into  $\text{CpW}(\text{CO})_3\text{Cl}$ .

#### Preparation of $\text{CpW}(\text{CO})_3\text{Cl}$ from $\text{W}(\text{CO})_6$

A mixture of  $\text{W}(\text{CO})_6$  (7.02 g, 20.0 mmol) and  $\text{CH}_3\text{CN}$  (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  $\text{CHCl}_3$  (10 ml) followed by  $\text{CCl}_4$  (12 ml) in a manner essentially identical to that described in the immediately preceding 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  $^1\text{H}$  nmr spectrum and infrared carbonyl stretching pattern.

## Results and Discussion

$\text{W}(\text{CO})_6$  has been converted into  $\text{CpW}(\text{CO})_3\text{Cl}$  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].



Based on reports by Keppie and Lappert [6] of low yields of  $\text{CpW}(\text{CO})_3\text{H}$  for reaction 3 in  $\text{CH}_3\text{CN}$  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.  $\text{CHCl}_3$  was added as a potential chlorine donor since it was unlikely to react with  $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$  but might react with the hydride  $\text{CpW}(\text{CO})_3\text{H}$ . Visual evidence (orange solution consistent with the presence of  $\text{CpW}(\text{CO})_3\text{H}$  [6] maintained for 3 h at 50 °C with  $\text{CHCl}_3$  present but lost within minutes when  $\text{CCl}_4$  added) suggests that little if any chlorination was due to  $\text{CHCl}_3$  [11].  $\text{CCl}_4$  was not added until  $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$  had apparently been completely converted into the hydride for fear of oxidiz-

ing the reactive zerovalent tris-acetonitrile complex.

Kubas [12] has recently reported that higher homologs of  $\text{CH}_3\text{CN}$  are superior to  $\text{CH}_3\text{CN}$  in convenience of preparation of  $\text{W}(\text{CO})_3(\text{RCN})_3$  from  $\text{W}(\text{CO})_6$  and in reactivity (solubility and ease of displacement of coordinated nitrile by incoming ligand). Our single-flask synthesis of  $\text{CpW}(\text{CO})_3\text{Cl}$  should be even simpler using propionitrile or butyronitrile. If the steric bulk of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CN}$  [13] (PrCN) makes it a sufficiently poor ligand, then it might be possible to prepare  $\text{CpW}(\text{CO})_3\text{H}$  from the crude reaction product mixture of  $\text{W}(\text{CO})_6$  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  $\text{CpW}(\text{CO})_3\text{Cl}$  upon addition of  $\text{CCl}_4$ .

The single-flask synthetic technique successful for  $\text{CpW}(\text{CO})_3\text{Cl}$  should be extendable to its halide analogs (instead of  $\text{CCl}_4$  as the halogenating agent for  $\text{CpW}(\text{CO})_3\text{H}$ ,  $\text{CHBr}_3$ ,  $\text{CBr}_4$ , or N-bromosuccinimide to afford the bromide and  $\text{CH}_2\text{I}_2$  or  $\text{CHI}_3$  to give the iodide) and the nitrosyl  $\text{CpW}(\text{NO})(\text{CO})_2$  (instead of  $\text{CCl}_4$ , the nitrosylating agent Diazald<sup>®</sup>, *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{N}(\text{CH}_3)\text{NO}$  [14]). The technique [15] might also be extended to preparation of the chromium and molybdenum analogs of the halides and nitrosyls, for  $\text{CpCr}(\text{CO})_3\text{H}$  and  $\text{CpMo}(\text{CO})_3\text{H}$  have been prepared from the respective hexacarbonyls via tris-acetonitrile intermediates [6].

## Acknowledgements

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## References

- [1]  $[\text{CpMo}(\text{CO})_3]_2$  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  $\text{Mo}(\text{CO})_6$  and cyclopentadiene in good yield: R. B. King and F. G. A. Stone, *Inorg. Syntheses*, 7, 99 (1963).
- [2] E. W. Abel, A. Singh and G. Wilkinson, *J. Chem. Soc.*, 1321 (1960).
- [3] A heated-tube reaction has afforded a 30% yield (based on W) of  $[\text{CpW}(\text{CO})_3]_2$  from  $\text{W}(\text{CO})_6$  and cyclopentadiene; G. Wilkinson, *J. Am. Chem. Soc.*, 76, 209 (1954).
- [4] D. P. Tate, W. R. Knipple and J. M. Augl, *Inorg. Chem.*, 1, 433 (1962).
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- [6] S. A. Keppie and M. F. Lappert, *J. Chem. Soc. (A)*, 3216 (1971).

- 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  $\text{CpW}(\text{CO})_3\text{Cl}$  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  $\text{CpMo}(\text{CO})_3\text{H}$  is converted in  $\text{CH}_3\text{CN}$  solution at 25 °C to  $\text{Mo}(\text{CO})_3(\text{CH}_3\text{CN})_3$  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  $\text{CpW}(\text{CO})_3\text{H}$  from  $\text{W}(\text{CO})_3(\text{CH}_3\text{CN})_3$  and excess CpH in  $\text{CH}_3\text{CN}$  in ref. 6.
- 11  $\text{CHCl}_3$  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  $\text{W}(\text{CO})_6$  than did its linear analog but provided no information as to whether  $\text{W}(\text{CO})_3(\text{i-PrCN})_3$  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  $\text{W}(\text{CO})_6$  to  $\text{CpW}(\text{CO})_3\text{Cl}$ .
- 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  $\text{CpMo}(\text{CO})_2(\text{NO})$  (ref. 7b) and  $\text{Rh}(\text{NO})(\text{PPh}_3)_3$  and  $\text{Ru}(\text{NO})_2(\text{PPh}_3)_2$  (J. J. Levison and S. D. Robinson, *Chem. Ind.*, 1514 (1969)).
- 15 Single-flask conversions of  $\text{Ru}_3(\text{CO})_{12}$  with CpH into  $\text{CpRu}(\text{CO})_2\text{X}$  (X = Cl, Br) (A. Eisenstadt, R. Tannenbaum and A. Efraty, *J. Organometal. Chem.*, **221**, 317 (1981)) and  $\text{CpRu}(\text{CO})(\text{PPh}_3)\text{Cl}$  (A. F. Humphries and S. A. R. Knox, *J. Chem. Soc. Dalton*, 1710 (1975)) have been reported.