ORGANOMETALLICS

Volume 1, Number 5, May 1982

Generation of Group 6 Metal Carbonyl Anions by Ion-Pair Extraction

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Received December 29, 1981

Phase transfer of hydroxide ion by quaternary ammonium salts in liquid–solid reactions leads to rapid and efficient syntheses of $HM(CO)_5^-$ and $HM_2(CO)_{10}^-$ (M = Cr, W) from the corresponding metal carbonyls. The technique can also be used to generate the cyclopentadienyl anion and provides an effective synthesis of η^5-$C_5H_5Mo(CO)_3^-$ from $Mo(CO)_6$.

Introduction

Nucleophilic additions of hydroxide ions to transition-metal carbonyl complexes have long been used as synthetic tools for the generation of metal carbonyl anions[1] and a variety of anionic products have been reported from reactions of hydroxide ion with group 6 metal carbonyls. The products range from the tris(μ-hydroxo) trianions,[2] $M_2(OH)_3(CO)_6^{3-}$ (M = Mo, W), to a μ-hydrido complex, $HCr_2(CO)_{10}^-$,[1e] and, most recently, to an alternate method for synthesis of the simple pentacarbonyl hydrides, $HM(CO)_5$– (M = Cr, Mo, W).[3] Hydroxide ion additions have also provided a method for oxygen-18 enrichment in $M(CO)_6$ derivatives.[4]

Noting that Makosza[5] and Zwierzak[6] have used quaternary ammonium salts as effective transfer agents for hydroxide in liquid–solid phase transfer catalyzed (LS-PTC) processes and having used quaternary ammonium ions ourselves recently[7] as stabilizing agents for a variety of metal carbonyl anions, it occurred to us that a liquid–solid method might provide an easy and economical route to some metal carbonyl anions.

Results and Discussion

The group 6 pentacarbonyl hydrides have been fully characterized recently, and a variety of methods have been reported for their synthesis.[3,8] These methods, although very effective, all have some undesirable features either in terms of the number of steps required in the synthetic sequences or the expense of reagents needed to convert $M(CO)_6$ to the product anions.

The method which we have developed for synthesis of $HM(CO)_5^-$ (M = Cr, W) from $M(CO)_6$ utilizes tetraethylammonium hydrogen sulfate as the phase-transfer agent together with powdered KOH.[9] The reaction times are short, and the product yields are good (see Table I). In addition to the pentacarbonyl hydride, each of the reaction mixtures also afforded a small quantity of a compound whose properties indicate that it is the binuclear dianion[10] $M_2(CO)_{10}^{2-}$; this product is readily separated from the pentacarbonyl hydride on the basis of solubility differences. Although the $HM(CO)_5^-$ complexes are certainly sensitive to water and suffer easy conversion to the corresponding μ-hydrides, we have found that some water is essential to make the reactions proceed at a reasonable rate. The effects of added water on the related LS-PTC reactions involving crown ether catalysts have been noted previously and are suggested to be due to the creation of a local liquid–liquid interface.[11] As with some other hydrido anions,[7b,12] treatment with halogenated solvents

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Table I. Reactions of Nucleophiles with Group 6 Metal Carbonyls by Ion-Pair Extraction

metal carbonyl	nucleophile	reaction time	product formed	product isolated	yield, %
$Cr(CO)_6$	OH^- [a]	30 min	$Et_4N^+HCr(CO)_5^-$	same	75
$Cr(CO)_6$	OH^- [b]	3 h	Et_4N^+-μ-$H[Cr(CO)_5]_2^-$	same	83
$W(CO)_6$	OH^- [a]	1 h	$Et_4N^+HW(CO)_5^-$	same	73
$W(CO)_6$	OH^- [b]	2 3/4 h	Et_4N^+-μ-$H[W(CO)_5]_2^-$	same	70
$Mo(CO)_6$	$C_5H_5^-$ [c]	3 h	*n*-$Bu_4N^+CpMo(CO)_3^-$	$CpMo(CO)_3SnPh_3$	80

[a] The PT agent was tetraethylammonium hydrogen sulfate. [b] The PT agent was tetraethylammonium bromide. [c] The PT agent was tetra-*n*-butylammonium hydrogen sulfate.

converts the pentacarbonyl hydrides to the corresponding haloanions $M(CO)_5X^-$.

When tetraethylammonium bromide is used as the phase-transfer agent, the type of product formed depends directly upon the availability of water. In the absence of added water, $M(CO)_5Br^-$ (M = Cr, W) is formed[13] whereas, with the addition of a small quantity of water, efficient syntheses of the μ-hydrides $HM_2(CO)_{10}^-$ result.

We have not attempted to use the liquid–solid method to synthesize either $HMo(CO)_5^-$ or $HMo_2(CO)_{10}^-$. The pentacarbonyl hydride has been described as thermally labile,[8b] and we have recently described the preparation of the μ-hydride from $Mo(CO)_6$ and Et_4NBH_4.[7b]

Originally, the anion $CpMo(CO)_3^-$ (Cp = η^5-C_5H_5) was prepared by the reaction of sodium cyclopentadienide with $Mo(CO)_6$.[14] Later it was prepared by reaction of dicyclopentadiene with $Mo(CO)_6$ followed by sodium amalgam reduction of the dimer $[CpMo(CO)_3]_2$.[15] More recent synthetic methods[16,7] have focused on improving the final reduction step in the second procedure but have not dealt with either the preparation of the dimer or reactions between the cyclopentadienyl anion and $Mo(CO)_6$.

Alper[17] has recently demonstrated the advantages of generating the cyclopentadienyl anion by liquid–solid phase-transfer catalysis (using 18-crown-6/KOH) in developing a method for the synthesis of some ferrocene derivatives. Since the older methods for the preparation of $CpMo(CO)_3^-$ are time consuming and inefficient and the newer ones are dependent upon the dimer, we have sought to make use of liquid–solid ion-pair extraction to provide a better route to this anion also. Our procedure again utilizes a quaternary ammonium salt as the phase-transfer agent and thus allows the isolation of a stable salt[18] or conversion of the anion into some derivative. The product yield is high and the overall reaction time is relatively short (see Table I).

Experimental Section

All reactions were carried out under an atmosphere of prepurified nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen; CH_3CN was distilled from P_2O_5 and stored under N_2 over molecular sieves. Hexane was treated with H_2SO_4 and distilled before use; CH_2Cl_2 was reagent grade and used directly. Dicyclopentadiene, tetraethylammonium bromide, triphenyltin chloride (recrystallized from benzene), and tetra-*n*-butylammonium hydrogen sulfate were obtained from Aldrich. Flake KOH (MCB) was powdered in a mortar under nitrogen (glovebag). The tetraethylammonium hydroxide (25% in CH_3OH) and $Mo(CO)_6$ were obtained from Alfa, and the $Cr(CO)_6$ and $W(CO)_6$ were obtained from Strem Chemicals; these chemicals were used as received.

Infrared spectra were recorded on a Perkin-Elmer Model 283 or 599B spectrophotometer and were calibrated against polystyrene film. ^1H NMR spectra were obtained on a Varian EM-390 spectrometer; peak positions are given in parts per million downfield (+) or upfield (–) from Me_4Si. Elemental analysis was performed by Galbraith Laboratories.

Preparation of $Et_4N^+HSO_4^-$.[19] Aqueous H_2SO_4 (47 mL of concentrated H_2SO_4 in 47 mL of water) was added dropwise with stirring to 400 mL of a 25% solution of Et_4NOH in methanol (0.84 mmol) cooled in an ice bath. After addition was complete, the mixture was stirred for an additional 2 h. The mixture was then concentrated on a rotary evaporator to an oily solid. The residue was then treated with 200 mL of CH_3CN and 500 mL of ether and stirred briefly. The product precipitated as white needles from this solvent mixture and was collected on a filtering funnel and washed several times with ether. After the precipitate was dried in a vacuum desiccator, the yield of product was 163.48 g (85%).

Preparation of $Et_4N^+HW(CO)_5^-$ and Conversion to $Et_4N^+W(CO)_5Br^-$. A mixture of $W(CO)_6$ (2.11 g, 6.0 mmol), powdered KOH (5.05 g, 90 mmol), and Et_4NHSO_4 (1.36 g, 6 mmol) was added directly under nitrogen to a three-necked 250-mL flask equipped with a mechanical stirrer, reflux condenser, and a Claisen adapter (to allow nitrogen purging and IR sampling). Acetonitrile, 80 mL, was then added to the flask followed by 0.4 mL of water under nitrogen. The mixture was then heated, with stirring, at 60 °C for 1 h. The solution gradually changed from yellow to orange and then back to yellow during this time, and IR spectra after 1 h indicated that $W(CO)_6$ had been consumed. The mixture was then cooled to room temperature, dried briefly with $MgSO_4$, and then filtered through celite into a Schlenk vessel. Solvent was removed under vacuum, and the residue was triturated with 30 mL of THF and then filtered. Hexane, 8 mL, was then added to the resulting solution, and this mixture was chilled (ice bath). A small amount of a semisolid material was removed by filtration, and its spectral properties indicated that it consisted primarily of the dianion $W_2(CO)_{10}^{2-}$: IR ν(CO) (CH_3CN) 1940 (w), 1890 (vs), 1865 (sh), 1770 (s) cm^{-1} [lit.[10] (KBr) 2010 (w), 1960 (sh), 1890 (vs), 1865 (sh), 1770 (s) cm^{-1}]. Solvents were removed from the filtrate, and the solid was collected, washed several times with hexane, and dried under vacuum. The resulting yellow-orange powder, 2.0 g (73%), had the following spectral properties: IR ν(CO) (CH_3CN) 1895 (s), 1860 (m) cm^{-1} [lit.[8b] ($PPN^+HW(CO)_5^-$) 2029 (vw), 1889 (s), 1858 (m) cm^{-1}]; ^1H NMR (CD_3CN) δ 1.25 (tt), 3.28 (q), –4.3 (J_{W-H} = 54.0 Hz) [lit.[8b] (CD_3CN) –4.2 (J_{W-H} = 53.4 Hz].

Treatment of 0.32 g (0.70 mmol) of the pentacarbonyl hydride with 0.36 g (1.42 mmol) of $CHBr_3$ in 25 mL of CH_3CN at room temperature effected its conversion to $Et_4N^+W(CO)_5Br^-$ after 20 min. Removal of solvent from the reaction mixture followed by drying under vacuum afforded 0.35 g (93%) of yellow powder: IR ν(CO) (CH_3CN) 2060 (w), 1915 (vs), 1845 (m) cm^{-1}. [lit.[13] (KBr)

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(18) The tetra-*n*-butyl salt could be isolated as an oil but could not be crystallized. In general, we have had more success in crystallizing tetraethylammonium salts of metal carbonyl anions than their tetra-*n*-butyl analogues.

(19) This method represents a modification of the procedures described previously; see C. M. Starks and C. Liotta, "Phase Transfer Catalysis", Academic Press, New York, 1978, Chapter 3.

2064 (w), 1904 (s), 1868 (m) cm^{-1}].

Preparation of $Et_4N^+HCr(CO)_5^-$ and Conversion to $Et_4N^+Cr(CO)_5Br^-$. A mixture of $Cr(CO)_6$ (2.65 g, 12 mmol), Et_4NHSO_4 (2.73 g, 12 mmol), and KOH (10.1 g, 180 mmol) were added to a 250-mL flask under nitrogen followed by 70 mL of CH_3CN and 0.4 mL of H_2O [the apparatus was the same as that described above for $Et_4N^+HW(CO)_5^-$]. After the mixture was heated at 60 °C for 30 min, an IR spectrum indicated that complete conversion of $Cr(CO)_6$ had occurred. The mixture was then cooled to room temperature, dried briefly with $MgSO_4$, and filtered through celite into a Schlenk vessel. Solvent was removed under vacuum, and the residue was triturated with 30 mL of THF and then filtered. Hexane (7 mL) was added to the filtrate and the mixture chilled briefly. The solid which precipitated was collected by filtration and amounted to 0.69 g (18%) of a yellow powder whose properties indicated that it was the dianion $Cr_2(CO)_{10}^{2-}$: IR ν(CO) (CH_3CN) (2060) (vw), 1912 (m), 1885 (vs), 1786 (m) cm^{-1} [lit.[10] (KBr) 2050 (w), 1960 (m), 1930 (vs), 1870 (s), 1740 (m) cm^{-1}]; treatment with water converted it to $HCr_2(CO)_{10}^-$. Solvent was removed from the filtrate under vacuum, and the residual orange solid was washed with several small portions of hexane and then dried under vacuum. The product, 2.9 g (75%), had the following spectral properties: IR ν(CO) (CH_3CN) 1885 (vs), 1850 (m) cm^{-1} [lit.[8a] (THF) 2023 (vw), 1892 (s), 1860 (m) cm^{-1}]; ^1H NMR (CD_3CN) δ 1.25 (tt), 3.20 (q), −7.00 (s) [lit.[8a] (CD_3CN) δ −7.00]. The product had the following analysis. Calcd for $C_{13}H_{21}O_5CrN$: C, 48.29; H, 6.55; N, 4.33. Found: C, 48.11, H, 6.64; N, 4.45.

Treatment of 0.28 g (0.86 mmol) of the pentacarbonyl hydride with 0.43 g (1.72 mmol) of $CHBr_3$ in 20 mL of CH_3CN at room temperature effected its conversion to $Et_4N^+Cr(CO)_5Br^-$ after 20 min. Removal of solvent from the reaction mixture followed by drying under vacuum afforded 0.33 g (99%) of yellow powder: IR ν(CO) (CH_3CN) 2060 (w), 1920 (vs), 1855 (m) cm^{-1} [lit.[13] (KBr) 2058 (w), 1906 (s), 1875 (m) cm^{-1}].

Preparation of $Et_4N^+HCr_2(CO)_{10}^-$. A mixture of $Cr(CO)_6$ (1.11 g, 5 mmol), KOH (2.52 g, 45 mmol), and Et_4NBr (1.05 g, 5 mmol) was prepared (under N_2) in a three-necked 250-mL flask equipped with a mechanical stirrer, a reflux condenser, and a Claisen adapter. Tetrahydrofuran, 80 mL, was then added to the flask followed by 0.2 mL of water. The mixture was then heated at 66 °C for 3 hours. After the mixture was cooled to room temperature, 10 mL of saturated brine solution was added and stirring was continued for a few minutes. The organic layer was then separated, and the aqueous layer was extracted several times with small portions of CH_2Cl_2. The combined organic extracts were then dried over $MgSO_4$ and filtered, and solvent was removed on a rotary evaporator. The crude product, 1.23 g of yellow powder, was recrystallized from THF–hexane at −70 °C under N_2; 1.07 g (83%) of yellow powder was obtained which had the following spectral properties: IR ν(CO) (THF) 2030 (w), 1940 (s), 1875 (m) cm^{-1} [lit.[10] ν(CO)(THF) 2033 (w), 1943 (vs), 1881 (s) cm^{-1}]; ^1H NMR (acetone-d_6) δ 1.38 (tt), 3.42 (q), −19.50 (s, Cr–H–Cr) [lit.[10] (THF) δ −19.47 (Cr–H–Cr)].

Preparation of $Et_4N^+HW_2(CO)_{10}^-$. In the manner described above for the chromium μ-hydride, a mixture of powdered KOH (0.67 g, 12 mmol), Et_4NBr (0.95 g, 4.5 mmol), 30 mL of THF, and 0.2 ml of water was stirred, mechanically, at room temperature for 15 min. A solution of $W(CO)_6$ (1.06 g, 3 mmol) in 50 mL of THF was then quickly added and the resulting mixture heated at 60 °C for 2.5 h. The solution was then cooled to room temperature, a small quantity of $MgSO_4$ was added, and the resulting mixture was filtered through celite. Solvent was removed on a rotary evaporator and 0.90 g of yellow powder remained. The crude product was recrystallized from CH_2Cl_2–hexane; the yield of pure product was 0.81 g (70%) of yellow powder. The product had the following spectral properties: IR ν(CO) (THF) 2040 (w), 1938 (s), 1880 (m) cm^{-1} [lit.[10] ν(CO) (THF) 2043 (w), 1943 (vs), 1880 (s) cm^{-1}]; ^1H NMR (acetone-d_6) δ 1.35 (tt), 3.50 (q), −12.50 (t, J_{W-H} = 42 Hz) [lit.[10] (THF) δ −12.52 (W–H–W (J_{W-H} = 41.9 Hz))].

Preparation of η^5-$C_5H_5Mo(CO)_3^-$ and Conversion to η^5-$C_5H_5Mo(CO)_3SnPh_3$. Freshly distilled cyclopentadiene (obtainbed from thermolysis of the dimer, 0.26 g, 2 mmol), powdered KOH (1.12 g, 20 mmol), and tetra-*n*-butylammonium hydrogen sulfate (2.04 g, 6 mmol) were mixed together in 30 mL of THF and heated with stirring to 66 °C. A solution containing $Mo(CO)_6$ (0.53 g, 2 mmol) in 30 mL of THF was then added dropwise during 1.5 h. Heating and stirring were continued for an additional 1.5 h; after this time, conversion to η^5-$C_5H_5Mo(CO)_3^-$ was complete as evidenced by an infrared spectrum of the mixture: ν(CO) 1900 (vs), 1780 (vs), 1765 (sh) cm^{-1} [lit.[20] for $Et_4N^+\eta^5$-$C_5H_5Mo(CO)_3^-$ 1885 (s), 1775 (s), 1740 (s) cm^{-1}]. The mixture was then cooled to room temperature and filtered, under N_2, through celite into a flask containing Ph_3SnCl (0.96 g, 2.5 mmol). The resulting solution was then stirred until conversion to the tin derivative was complete (1.5 h). The solution was then washed with brine, dried over $MgSO_4$, and filtered. Solvent was removed on a rotary evaporator, and the crude product was recrystallized from CH_2Cl_2–hexane. The yield of η^5-$C_5H_5Mo(CO)_3SnPh_3$ was 0.95 g (80%): IR ν(CO) (THF): 2000 (vs), 1930 (m), 1900 (vs) cm^{-1} [lit.[21] (CCl_4) 2004, 1934, 1909].

Acknowledgment. We thank the Graduate School Research Council of the University of Louisville for financial support of this project. K.R.P. gratefully acknowledges a summer fellowship from the National Science Foundation (Grant RIAS-77-06911). We also thank the National Science Foundation (Grant CHE-79-26044) for providing matching funds for the purchase of the Perkin-Elmer 599B infrared spectrophotometer.

Registry No. $Et_4N^+HCr(CO)_5^-$, 77110-93-1; Et_4N^+-μ-$H[Cr(CO)_5]_2^-$, 16924-36-0; $Et_4N^+HW(CO)_5^-$, 80907-47-7; Et_4N^+-μ-$H[W(CO)_5]_2^-$, 19033-39-7; *n*-$Bu_4N^+CpMo(CO)_3^-$, 61618-13-1; $CpMo(CO)_3SnPh_3$, 12100-85-5; $Cr(CO)_6$, 13007-92-6; $W(CO)_6$, 14040-11-0; $Mo(CO)_6$, 13939-06-5; $Et_4N^+W(CO)_5Br^-$, 14780-94-0; $Et_4N^+Cr(CO)_5Br^-$, 14780-93-9; $Et_4N^+HSO_4^-$, 16873-13-5; Et_4NBr, 71-90-0; KOH, 1310-58-3; $W_2(CO)_{10}^{2-}$, 45264-18-4; $Cr_2(CO)_{10}^{2-}$, 45264-01-5.

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