

Anionic Group 6B Metal Carbonyl Hydrides and Formates. Chemistry Relevant to Catalysis of the Water Gas Shift Reaction by Group 6B Metal Hexacarbonyls[†]

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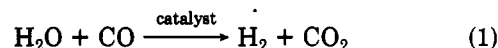
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The reaction of cryptand (kryptofix-222) solubilized KOH with the group 6B metal hexacarbonyls in aprotic solvents to afford the $M(CO)_5H^-$ anions is described. Subsequent facile insertion reactions of these hydridic metal complexes with CO_2 , COS, and CS_2 have provided routes to the corresponding metalloformate, -thioformate, and -dithioformate derivatives. Alternatively, the $M(CO)_5O_2CH^-$ derivatives were synthesized from the $M(CO)_5Y^-$ ($Y = Cl, I$) anions and TiO_2CH . These salts were all fully characterized by ^{13}C and 1H NMR and infrared spectroscopy. The bonding mode in the thioformate species was shown to be through the sulfur atom as revealed by X-ray crystallography on the chromium analogue. Crystals of $[PPN][Cr(CO)_5SC(O)H]$ were found to belong to the triclinic space group $P\bar{1}$ with $a = 12.671(5) \text{ \AA}$, $b = 12.880(5) \text{ \AA}$, $c = 15.356(6) \text{ \AA}$, $\alpha = 108.01(3)^\circ$, $\beta = 119.61(3)^\circ$, $\gamma = 97.48(3)^\circ$, $Z = 2$. $R = 4.0\%$ for 5811 reflections with $I > 3\sigma(I)$. Decarboxylation of the $M(CO)_5O_2CH^-$ derivatives to provide $M(CO)_5H^-$ and CO_2 was observed, with the $Cr(CO)_5O_2CH^-$ species undergoing CO_2 extrusion much more readily than its tungsten counterpart. This decarboxylation process was shown to proceed via CO dissociation; i.e., it was inhibited in the presence of carbon monoxide. Unlike their formate analogues, the thioformate derivatives displayed no tendency to extrude COS or CS_2 with concomitant $HM(CO)_5^-$ formation. ^{13}C -labeling experiments demonstrated that the intermediate afforded from OH^- addition to $M(CO)_6$, $M(CO)_5COOH^-$, and its structural isomer, $M(CO)_5O_2CH^-$, do not interconvert by an intramolecular process. A discussion of the roles of $M(CO)_5COOH^-$ and $M(CO)_5O_2CH^-$ intermediates in the foremost mechanistic step in the catalysis of the water gas shift reaction by group 6B metal hexacarbonyls in alkaline media is included.

Introduction

Reactions of the group 6B metal hexacarbonyls with potassium hydroxide were studied initially by Hieber and co-workers in the late fifties.¹ These studies were carried out in protic solvents at elevated temperatures ($>65^\circ C$). In general the base reactions of the $M(CO)_6$ ($M = Cr, Mo, W$) complexes in KOH-methanol gave binuclear anions whose structures are still somewhat unclear but were suggested to contain hydroxo or methoxo bridges as well as OH^- and CH_3OH ligands in addition to CO .² The structures of the potassium salts of one of the products of alkaline hydrolysis of $M(CO)_6$ ($M = Mo, W$), tris(μ -hydroxo)hexacarbonyldimetallate(0) trianion, have been reported.^{1,3} On the other hand its protonated counterpart is believed to be the tetramer $[M(OH)(CO)_3]_4(H_3O)_4$, which is formulated as a (μ_3 -hydroxo)metal compound.⁴ For the reaction of $Cr(CO)_6$ with hydroxide ion the intermediacy of the $HCr(CO)_5^-$ anion was suspected.⁵ Since all of the investigations lacked definitive spectroscopic identification, we have elected to reexamine the reaction processes in both protic and aprotic solvents. It was anticipated that these base reactions could be studied in the absence of many of the secondary complicating features noted in earlier efforts by utilizing aprotic conditions. Modifications of the reaction process to take adequately into account the effects of protic solvents were subsequently incorporated into the scheme. Our studies were aided by the recent spectral data reported by our colleagues⁶ for the analytically pure metal pentacarbonyl hydride anions obtained by protonation of $M(CO)_5^{2-}$.

The impetus for the intense interest in these investigations stems from efforts designed to understand more fully the individual steps in the homogeneous catalysis of the water-gas shift reaction (WGSR), eq 1, in the presence



of group 6B metal hexacarbonyls in alkaline solution.⁷⁻⁹ Indeed, the reaction of hydroxide ion with mononuclear and cluster metal carbonyl catalysts is in general a pivotal step in the eventual production of hydrogen via eq 1.¹⁰

An additional aim of this present contribution is to elaborate mechanistically on the reaction between one of the products of the WGSR, CO_2 , and the anionic metal hydride intermediates present during the catalytic cycle (eq 2);¹¹

- (1) (a) Hieber, W.; Abeck, W.; Platzer, H. K. *Z. Anorg. Allg. Chem.* 1955, 280, 241. (b) Hieber, W.; Rieger, K. *Ibid.* 1959, 300, 288. (c) Hieber, W.; Englert, K.; Rieger, K. *Ibid.* 1959, 300, 295. (d) Hieber, W.; Englert, K. *Ibid.* 1959, 300, 304.
- (2) See, e.g., the review by F. Calderazzo in: Wender, I.; Pino, P. "Metal Carbonyls in Organic Synthesis"; Interscience, New York, 1968.
- (3) Albana, V. G.; Ciani, G.; Manassero, M. *J. Organomet. Chem.* 1970, 25, C55.
- (4) Albana, V.; Bellon, P.; Ciani, G.; Manassero, M. *Chem. Commun.* 1969, 1242.
- (5) Hieber, W.; Beck, W.; Braun, G. *Angew. Chem.* 1960, 72, 795 and references cited therein.
- (6) (a) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* 1981, 20, 1644. (b) Darensbourg, M. Y.; Slater, S. J. *Am. Chem. Soc.* 1981, 103, 5914.
- (7) Darensbourg, D. J.; Darensbourg, M. Y.; Burch, R. R., Jr.; Froelich, J. A.; Incorvia, M. J. *Adv. Chem. Ser.* 1979, No. 173, 106.
- (8) Darensbourg, D. J.; Baldwin, B. J.; Froelich, J. A. *J. Am. Chem. Soc.* 1980, 102, 4688.
- (9) Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.* 1981, No. 152, 107.
- (10) (a) Laine, R. M.; Rinker, R. G.; Ford, P. C. *J. Am. Chem. Soc.* 1977, 99, 252. (b) Cheng, C. H.; Hendriksen, D. E.; Eisenberg, R. *Ibid.* 1977, 99, 2791. (c) Kang, H.; Mauldin, C. H.; Cole, T.; Slegeir, W.; Cann, K.; Pettit, R. *Ibid.* 1977, 99, 8323. (d) King, R. B.; Frazier, C. C.; Hanes, R. M.; King, A. D. *Ibid.* 1978, 100, 2925. (e) Frazier, C. C.; Hanes, R.; King, A. D.; King, R. B. *Adv. Chem. Ser.* 1979, No. 173, 94. (f) Pettit, R.; Cann, K.; Cole, T.; Mauldin, C. H.; Slegeir, W. *Ibid.* 1979, No. 173, 121. (g) Singleton, T. C.; Park, L. J.; Price, J. C.; Forster, D. *Prepr. Div. Pet. Chem., Am. Chem. Soc.* 1979, 24, 329. (h) Laine, R. M. *J. Am. Chem. Soc.* 1978, 100, 6451. (i) Baker, E. C.; Hendriksen, D. E.; Eisenberg, R. *Ibid.* 1980, 102, 1020. (j) King, A. D.; King, R. B.; Yang, D. B. *Ibid.* 1980, 102, 1028. (k) Ungermann, C.; Landis, V.; Moya, S. A.; Cohen, H.; Walker, H.; Pearson, R. G.; Rinker, R. G.; Ford, P. C. *Ibid.* 1979, 101, 5922.

[†] Dedicated to the memory of Professor Rowland Pettit.

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and to characterize fully the anionic (formate)metal derivatives hence derived. The reduction of CO_2 by means of reaction 2 represents an important preliminary process in the production of reduced carbon-containing molecules such as alcohols and hydrocarbons from carbon dioxide feedstocks. Insertion reactions involving the analogous sulfur-containing triatomic molecules, COS and CS_2 , are also reported herein.

Experimental Section

Materials. Thallium(I) formate, bis(triphenylphosphine)iminium chloride, and $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) were purchased from Alfa Products and Strem Chemicals, respectively. Mallinckrodt analytical reagent grade KOH was used. CO, COS, and CO_2 were obtained from Matheson and were used without further purification. Carbon monoxide enriched to 91.6% in ^{13}C , carbon dioxide enriched to 91.6% in ^{13}C , and carbon disulfide enriched to 91% in ^{13}C isotope were supplied by Prochem, B.O.C. Ltd., London. 4,7,13,16,21,24-Hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane (crypt-222, kryptofix-222) was supplied by Parish Chemicals, Provo, UT. Dichloromethane and acetonitrile were dried by refluxing with phosphorus pentoxide followed by distillation. Hexane, 1,2-dimethoxyethane, and tetrahydrofuran were dried by refluxing over Na benzophenone and followed by distillation. All reactions were carried out under an atmosphere of dry nitrogen in standard Schlenk ware.

Preparation of [K-kryptofix-222] $^+$ OH $^-$ Solution. In a typical experiment a mixture of 2.0 g (37.7 mmol) of KOH and 0.92 g of kryptofix-222 was vigorously stirred in 70 mL of freshly distilled CH_3CN at room temperature for 24 h. The colorless solution was filtered under nitrogen, and the remaining white dusty solid was washed three times with 10 mL of CH_3CN . Combined solutions were used in further experiments by assuming $[\text{OH}^-] = 0.0244 \text{ M}$ as equal to the concentration of cryptand.

Preparation of [K-kryptofix-222] $^+$ [HM(CO) $_5$] $^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). All syntheses of these species were performed in a similar manner. In a typical preparation 0.088 g of $\text{Cr}(\text{CO})_6$ (0.40 mmol) was dissolved in 33 mL of the [K-kryptofix-222] $^+$ [OH] $^-$ -MeCN solution, and a homogeneous yellow solution was obtained. The reaction was complete within minutes at room temperature as indicated by the infrared spectrum in the carbonyl region. Within the next 2–3 h precipitation of a white solid was observed. The solid was centrifuged from the solution, and its ^{13}C NMR spectrum in D_2O -2-ethoxyethanol mixture was recorded. The IR spectrum of the yellow solution remained unchanged after precipitation of the solid. The solution was used in further experiments directly, or the solvent was stripped off under reduced pressure and the resulting yellow solid was redissolved in dry CD_3CN for ^1H and ^{13}C NMR spectral analysis.

Preparation of [K-kryptofix-222] $^+$ [(CO) $_5$ MXHY] $^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{Y} = \text{X} = \text{O}$; $\text{X} = \text{Y} = \text{S}$; $\text{X} = \text{S}, \text{Y} = \text{O}$). All syntheses of these compounds were carried out in a completely analogous manner. In a typical experiment 2 mL of the [K-kryptofix-222] $^+$ [HM(CO) $_5$] $^-$ solution (obtained as described above) reacted at ambient temperature with an excess of CO_2 , COS (purging or pressurizing the solution), or CS_2 (synting into solution) while being stirred. IR and/or NMR analyses were performed on the solution ~5 min after the reaction began.

Preparation of [M(CO) $_5$ OCHO]PPN $^+$ or -Et $_4$ N $^+$. In a typical synthesis [PPN] $^+$ [W(CO) $_5$ Cl] $^-$ (1.8 g, 2 mmol) was allowed to react with TIOCHO (0.75 g, 3 mmol) in 50 mL of DME. The mixture was stirred for 1 h at room temperature and filtered through Celite under nitrogen. To the filtrate was added 60 mL of hexane, resulting in formation of a yellow-brown oil. When the oil was washed repeatedly with hexane, 1.1 g (~61%) of a yellow solid product was obtained. The chromium and molybdenum derivatives were prepared similarly by using CH_2Cl_2 as a solvent.

Preparation of [M(CO) $_5$ SCHY] $^-$ PPN $^+$ or -Et $_4$ N $^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{Y} = \text{O}, \text{S}$). All the syntheses were carried out in a similar

manner, i.e., allowing the $[\text{M}(\text{CO})_5\text{OCHO}]\text{PPN}^+$ or -Et $_4$ N $^+$ salt to react with excess COS or CS_2 . In a representative experiment $[\text{Cr}(\text{CO})_5\text{OCHO}][\text{PPN}]$ (0.50 g, 0.65 mmol) was dissolved in 2.5 mL of CD_3CN . The solution was syringed through a septum into a 25-mL Schlenk flask fitted with COS and was pressurized with COS (~20 kPa). The solution was left stirring at room temperature for ~16 h and decompressed and its ^{13}C NMR spectrum recorded. The solution was next filtered under nitrogen through Celite and cooled to ~-20 °C to afford 0.32 g (~0.40 mmol or 63%) of brown-yellow crystals.

The molybdenum and tungsten derivatives were prepared in a completely analogous manner with the only difference being longer reaction times, Mo, ~3 days, and W, ~1 week.

^{13}CO Exchange Reactions in [M(CO) $_5$ XHY] $^-$ [PPN] $^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{X} = \text{Y} = \text{O}$; $\text{X} = \text{Y} = \text{S}$; $\text{X} = \text{S}, \text{Y} = \text{O}$). These reactions were carried out in Schlenk storage tubes (10-mL capacity) under an atmosphere of 20 kPa of ^{13}CO (91.6% of ^{13}C) in THF solvent. The tubes were fitted with septum caps secured by copper wire and were equipped with stirring bars. The reactions were performed at room temperature by using 2.2 mL of 0.01 M solutions of the formate salts. Samples were withdrawn at regular time intervals with a hypodermic syringe for infrared analysis.

The same technique was used to prepare samples for ^{13}C NMR analysis employing 0.10 M solutions of the formate salts in CD_3CN .

$^{13}\text{CO}_2$ Exchange Reactions in [M(CO) $_5$ OCHO] $^-$ [PPN] $^+$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$). These reactions were carried out by using the same technique which was used in the ^{13}CO exchange reactions described above. A 2.2-mL sample of a 0.10 M solution of the formate salt in CD_3CN was allowed to react with $^{13}\text{CO}_2$ (91.6% of ^{13}C) at 20 kPa for 1 h at room temperature. The ^{13}C NMR spectrum of this solution was then recorded.

Infrared Spectra. The infrared spectra were recorded in 0.1-mm matched sealed NaCl cells on a Perkin-Elmer 283B spectrophotometer equipped with an Infrared Data Station and employing the PECDS software package provided by Perkin-Elmer. The spectra were calibrated against a water vapor spectrum below 2000 cm^{-1} and against a CO spectrum above 2000 cm^{-1} .

^{13}C NMR Spectra. The ^{13}C NMR spectra were recorded on a JEOL FX60 spectrometer operated at 15.03 MHz with an internal deuterium lock. Samples were run in CD_3CN solvent in 10-mm tubes. Spectra were determined employing a sweep width of 4 KHz (16K data block) with an acquisition time of 2 s, a pulse repetition rate of 5 s, and a flip angle of 30°.

The methyl carbon of deuterioacetonitrile was used as an internal standard. The chemical shift $\delta_{\text{CD}_3\text{CN}}$ 0.36 has been assigned to it on the basis of the ^{13}C NMR spectrum of a CD_3CN -MeOH mixture. This value was used, instead of $\delta_{\text{CD}_3\text{CN}}$ 1.3 reported in the literature, since the chemical shifts of other reactants (CO, CO_2 , CS_2) obtained by using it as a reference were in agreement with literature data.

^1H NMR Spectra. The ^1H NMR spectra were measured on a Varian EM-390 spectrometer in CD_3CN solutions with Me_4Si as reference.

Crystallographic Studies. Crystallographic analyses were carried out by Dr. Cynthia S. Day at Crystalitics Co. (Lincoln, NE). An irregular-shaped yellow crystal, minimum and maximum dimensions of 0.68 and 0.93 mm, respectively, was sealed under nitrogen in a thin-glass capillary with its longest dimension nearly parallel to the phi axis of the instrument. The crystal was then accurately centered optically on a computer-controlled four-circle Nicolet autodiffractometer, and a total of 15 high-angle ($2\theta_{\text{MoK}\alpha} > 30^\circ$) reflections were used to align the crystal and calculate angular settings for each reflection. A least-squares refinement of the diffraction geometry for these 15 reflections recorded at ambient laboratory temperature of $20 \pm 1^\circ\text{C}$ with graphite-monochromated Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) showed the crystal to belong to the triclinic system with lattice constants $a = 12.671(5) \text{ \AA}$, $b = 12.880(5) \text{ \AA}$, $c = 15.356(6) \text{ \AA}$, $\alpha = 108.01(3)^\circ$, $\beta = 119.61(3)^\circ$, and $\gamma = 97.48(3)^\circ$. Systematic absences indicated the space group to be $P\bar{1}-C_1^1$ (No. 2).¹² A unit cell of two $[\text{Cr}(\text{CO})_5\text{SC}(\text{O})\text{H}][\text{NP}_2(\text{C}_6\text{H}_5)_6]$ molecules per 1947 (1) $\text{\AA}^3$ afforded

(11) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* 1981, 103, 3223.

(12) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. I.

Table I. IR and NMR Data of the Metal Pentacarbonyl Hydride Anions Produced in the Reaction

$$\text{M}(\text{CO})_6 + 2\text{OH}^- \xrightarrow{2[\text{K-crypt}]^+} \text{M}(\text{CO})_5\text{H}^- + \text{HCO}_3^-$$

M	$\nu(\text{CO}), ^a \text{cm}^{-1}$			$^1\text{H NMR}, ^b \tau$	$^{13}\text{C NMR}, ^b \text{ppm}$	
	$A_1(2)$	$A_1(1)$	E		$\delta(\text{C}_{\text{eq}})$	$\delta(\text{C}_{\text{ax}})$
Cr	2023 vw	1857 m	1888 s	17.0	227.7 ^c	231.4 ^c
Mo	2036 vw	1864 m	1898 s	14.8	215.4	219.5
W	2036 vw	1858 m	1892 s	14.0	205.3 ^d	209.6

^a Frequencies were measured in CH_3CN solution and are accurate to $\pm 2 \text{ cm}^{-1}$. ^b In CD_3CN . ^c At temperature $\leq -6^\circ \text{C}$, at room temperature one signal at $\sim 228.7 \text{ ppm}$; $J^{13}\text{C}_{\text{ax}}\text{-Cr-}^{13}\text{C}_{\text{eq}} = 5.86 \text{ Hz}$. ^d $J_{\text{W-C}} = 124.02 \text{ Hz}$.

a calculated density of 1.35 g cm^{-3} . The linear absorption coefficient of the crystal for Mo $K\alpha$ radiation is 0.49 mm^{-1} .^{13a}

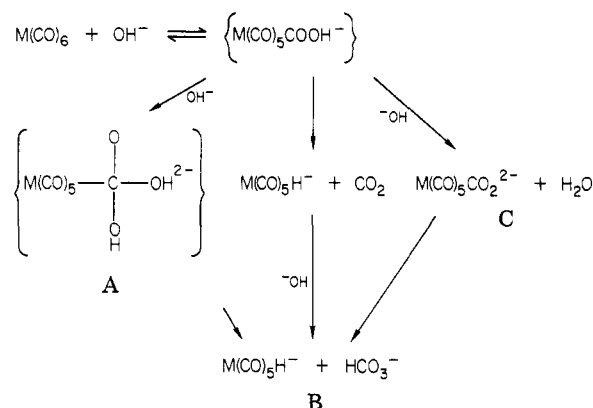
Intensity measurements utilized graphite-monochromated Mo $K\alpha$ radiation and the ω scanning technique with a 4° takeoff angle and a normal-focus X-ray tube. A total of 8945 independent reflections having $2\theta \leq 55^\circ$ were measured in two shells. A scanning rate of $6.0^\circ/\text{min}$ was employed for the scan between settings 0.50° respectively above and below the calculated $K\alpha$ doublet value for those reflections having $3.0^\circ < 2\theta_{\text{MoK}\alpha} \leq 43.0^\circ$, and a scanning rate of $4.0^\circ/\text{min}$ was used for reflections having $43^\circ < 2\theta_{\text{MoK}\alpha} \leq 55.0^\circ$. Each of these 0.90° scans was divided into 19 equal time intervals, and those 13 contiguous intervals which had the highest single accumulated count at their midpoint were used to calculate the net intensity from scanning. Background counts, each lasting for one-fourth the total time used for the net scan, were measured at ω settings 0.90° above and below the calculated value for each reflection. The six standard reflections, measured every 400 reflections as a monitor for possible disalignment and/or deterioration of the crystal, gave no indication of either. The intensity data were corrected empirically for absorption effects using psi scans for six reflections having 2θ between 8 and 30° and were then reduced to relative squared amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

Of the 8945 reflections examined, 3134 were eventually rejected as unobserved by applying the rejection criterion, $I < 3.0\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity computed from $\sigma^2(I) = (C_i + k^2B)$ where C_i is the total scan count, k is the ratio of scan time to background time, and B is the total background count.

The position for the Cr atom was derived by using the SHELXTL direct methods software from Nicolet; the 52 remaining non-hydrogen atoms appeared in a single difference Fourier synthesis based on refined parameters for the chromium atom [$R_1 = 0.542$ for 3571 independent reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ and $I > 3\sigma(I)$]. Isotropic unit-weighted full-matrix least-squares refinement for the 53 non-hydrogen atoms gave R_1 (unweighted, based on F) = 0.90 and R_2 (weighted) = 0.088 where anisotropic refinement $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = \{ \sum w(|F_o| - |F_c|)^2 / \sum |F_o|^2 \}^{1/2}$ converged to $R_1 = 0.056$ and $R_2 = 0.060$ for 3571 reflections having $2\theta_{\text{MoK}\alpha} < 43^\circ$ and $I > 3\sigma(I)$.¹⁴ These and all subsequent structure factor calculations employed the atomic form factors compiled by Cromer and Mann¹⁵ and an anomalous dispersion correction to the scattering factors of the chromium, sulfur, and phosphorus atoms.^{13b}

The position for the hydrogen atom of the $\text{SC}(\text{O})\text{H}$ ligand was derived from a difference Fourier. The hydrogen positions for the $(\text{NP}_2(\text{C}_6\text{H}_5)_6)$ cation were calculated by using idealized sp^2 -hybridized geometry. All cation hydrogen atoms were assigned isotropic thermal parameters of $5.0 \text{ \AA}^2$; positional parameters and temperature factors for the cation hydrogen atoms were not varied during the remaining cycles of least-squares refinement. Further unit-weighted least-squares refinement with those reflections having $2\theta_{\text{MoK}\alpha} < 55.0^\circ$, which employed an isotropic thermal parameter for the hydrogen atom of the $\text{SC}(\text{O})\text{H}$ ligand but was

Scheme I



otherwise anisotropic, gave $R_1 = 0.041$ and $R_2 = 0.039$ for 5811 reflections having $I > 3\sigma(I)$.

The final cycle of empirically weighted^{16,17} least-squares refinement which employed isotropic thermal parameters for hydrogen atoms and anisotropic thermal parameters for all others converged to $R_1 = 0.040$, $R_2 = 0.048$, and $\text{GOF} = 1.3$ ¹⁸ for 5811 reflections. During the final cycle of refinement, no parameter (including those of the hydrogen atom) shifted by more than $0.31\sigma_p$ with the average shift being less than $0.04\sigma_p$ where σ_p is the estimated standard deviation of the parameter. There were no peaks present in the final difference Fourier above the noise level ($0.31 \text{ e/\AA}^3$).

All calculations were performed on a Data General Eclipse S-200 computer with 64K of 16-bit words, a parallel floating-point processor for 32- and 64-bit arithmetic, and a Data General disk with 10-million 16-bit words using versions of the Nicolet (Syntex) E-XTL or SHELXTL interactive crystallographic software package as modified at Crystallitics Co.

Results and Discussion

We have previously shown that the principal metal carbonyl components in an alkaline 2-ethoxyethanol solution of a WGS catalyst prepared from $\text{Cr}(\text{CO})_6$ were $\text{Cr}(\text{CO})_6$ and $\text{Cr}(\text{CO})_5\text{H}^-$.⁹ However, the reactivity of hydroxide ion toward the metal hexacarbonyls depends strongly on the reaction conditions. The reaction of hydroxide ions with $\text{Cr}(\text{CO})_6$ in aqueous 2-ethoxyethanol to afford $\text{Cr}(\text{CO})_5\text{H}^-$ occurs very slowly (~ 1 week) at 40°C , even in the presence of a 30-fold excess of hydroxide, with concomitant formation of $\text{H}[\text{Cr}(\text{CO})_5]_2^-$.¹⁹ Raising the temperature to 100°C brings about fast consumption (20 min) of chromium hexacarbonyl, but along with the predominant products, $\text{Cr}(\text{CO})_5\text{H}^-$ and $\text{H}[\text{Cr}(\text{CO})_5]_2^-$, some

(16) The weighting scheme used in the least-squares minimization of the function $\sum w(|F_o| - |F_c|)^2$ is defined as $w = 1/\sigma_F^2$.

(13) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol IV: (a) pp 55-66; (b) pp 149-150.

(14) The anisotropic thermal parameter is of the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}k lb^*c^*)]$.

(15) Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A* 1968, A24, 321.

(17) For empirical weights $\sigma_F = \sum a_n |F_o|^n = a_0 + a_1 |F_o| + a_2 |F_o|^2 + a_3 |F_o|^3$, with the a_n being coefficients from the least-squares fitting of the curve $|F_o| - |F_c| = \sum a_n |F_o|^n$. In this case $a_0 = 0.589$, $a_1 = -7.47 \times 10^{-3}$, $a_2 = 3.64 \times 10^{-4}$, and $a_3 = -1.65 \times 10^{-6}$.

(18) $\text{GOF} = \{ \sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV}) \}^{1/2}$, where NO is the number of observations and NV is the number of variables.

(19) See ref 6 for the explanation for the formation of the $\text{H}[\text{Cr}(\text{CO})_5]_2^-$ species.

Table II. Spectroscopic Data for Metal Pentacarbonyl Formate Derivatives of Group 6B Metals

substi- tuent	cation	M	IR of carbonyl region, ^a cm ⁻¹					¹ H NMR ^b			¹³ C NMR ^b			
			A ₁ (²)	A ₁ (¹)	E	B ₁	k ₁	k ₂	δ	¹ J _{CH} , Hz ^c	δ _{ax}	δ _{eq}	δ _{sub}	¹ J _{CH} , Hz ^d
OCHO	K-crypt ^e	Cr	2056	1858	1925		14.09	15.63	8.28	190.5	222.6 ^f	216.1 ^f	167.9	190.4
		Mo	2066	1850	1927	1979	13.98	15.70	8.23		216.4	205.9		
		W	2064	1851	1915	1966	14.02	15.56	7.95		205.0	200.2 ^g	167.3	
	PPN	Cr	2056	1850	1918	1968	13.98	15.55			222.8	216.1	167.3	189.9
		Mo	2062	1849	1919	1970	13.97	15.59			216.1	205.8	167.1	190.9
		W	2061	1848	1909	1958	13.98	15.48			205.0	200.2 ^g	167.4	193.9 ^h
SCHO	K-crypt	Cr	2051	1865	1921	1977	14.20	15.55	10.54		225.7	219.1	...	...
		Mo	2063	1965	1928		14.21	15.69	10.50					
		W	2063	1862	1919	1969	14.18	15.59	10.47		204.1	199.6	198.4	
	PPN	Cr	2053	1866	1920	1969	14.22	15.55	10.52		225.8	219.1	198.8	185.6
		W	2056	1856	1913		14.09	15.49			204.2	199.8 ⁱ	198.3	187.5
		Mo	2054	1881	1925	1972	14.45	15.61	11.74	172.5	225.5 ^f	218.1 ^f	239.3	172.4
SCHS	K-crypt	Cr	2054	1881	1925	1972	14.45	15.61	11.74	172.5	225.5 ^f	218.1 ^f	239.3	172.4
		Mo	2061	1875	1930	1980	14.36	15.70						
		W	2062	1871	1921	1971	14.31	15.61			204.3	199.3	237.4	173.8
	PPN	Cr	2053	1874	1922	1969	14.35	15.57	11.80	172.5	225.3	218.0	239.2	171.9
		Mo	2058	1861	1923	1967	14.15	15.61	11.85					
		W	2057	1864	1915	1963	14.21	15.52	11.70	172.5	204.2	199.5 ^j	237.9	173.8

^a K-crypt salts in CH_3CN and PPN salts in THF. ^b Run in CD_3CN . ^c Carboxylic group specifically ^{13}C enriched. ^d Applying gated 1 pulse sequence. ^e K^+ encapsulated in kryptofix-222. ^f These two sets of numbers were mistakenly interchanged in our communication¹¹ concerning this subject. A subsequent correction was submitted to the editor of *J. Am. Chem. Soc.* ¹ $J_{\text{Cax-Cr-}^{13}\text{Ceq}} = 5.86 \text{ Hz}$. ^g $^1J_{\text{W-C}} = 130.4 \text{ Hz}$. ^h $^1J_{\text{C-D}} = 29.5 \text{ Hz}$. ⁱ $^1J_{\text{W-C}} = 128.4 \text{ Hz}$. ^j $^1J_{\text{W-C}} = 127.0 \text{ Hz}$.

unidentified carbonyl metalates are observed.²⁰ Under the conditions where OH^- is not hydrated, KOH in THF or CH_3CN with cryptand (crypt-222), the reaction is much faster and cleaner affording $\text{Cr}(\text{CO})_5\text{H}^-$ within minutes at ambient temperature. These observations are indicative of the importance of ion pairing in nucleophilic addition reactions involving metal carbonyls.^{21,22}

The reaction of cryptate-solubilized KOH in aprotic solvents with the hexacarbonyls of the group 6B metals was found to be dependent on the molar ratio of the reactants. When a twofold or larger excess KOH to hexacarbonyl was used, the reaction produced within minutes the corresponding $\text{HM}(\text{CO})_5^-$ anion. The spectral data presented in Table I for the $\text{HM}(\text{CO})_5^-$ salts obtained by this method are identical with that published for these species synthesized by protonation of $\text{M}(\text{CO})_6^{2-}$.⁶ For molar ratios of reactants ($\text{KOH-M}(\text{CO})_6$) less than 2, unreacted $\text{M}(\text{CO})_6$ is present in the reaction mixture along with the $\text{HM}(\text{CO})_5^-$ anion. Scheme I represents processes that are all consistent with the observed stoichiometry of the reaction.

The oxygen-18 labeling experiments showed that the metalcarboxylic acid derivatives have a long enough lifetime to effect oxygen exchange prior to anionic metal hydride formation. Indeed in the reactions of $\text{W}(\text{CO})_6$ and $\text{Mo}(\text{CO})_6$ with KOH-crypt-222 in THF we have some spectral evidence for the existence of transient metalcarboxylic acid species. For example, monitoring the reaction of $\text{W}(\text{CO})_6$ with OH^- in THF at -25°C by means of ^{13}C NMR spectroscopy reveals the presence of an intermediate with resonances of the appropriate intensity ratio at 205.3 ppm ($\delta(\text{C}_{\text{ax}})$) and 201.1 ppm ($\delta(\text{C}_{\text{eq}})$)²³ which

in time collapse into those assignable to $\text{HW}(\text{CO})_5^-$. In addition, a transitory infrared band in the $\nu(\text{CO})$ region at 1912 cm^{-1} (other anticipated weaker bands were masked by those of $\text{HW}(\text{CO})_5^-$) was observed.²³

Addition of a second hydroxide base to the carboxylic carbon atom of the metalcarboxylic acid (route A) or to another carbonyl ligand to afford a dicarboxylic acid anion²⁴ seems more likely than process B²⁵ since no evidence of contamination of the metal pentacarbonyl hydride anions with the corresponding formate derivatives was noted. That is, the $\text{HM}(\text{CO})_5^-$ anions are very reactive toward CO_2 with production of $\text{HCO}_2\text{M}(\text{CO})_5^-$ derivatives (vide infra).¹¹ Pathway C for decarboxylation of the metalcarboxylic acid appears less likely as well under these aprotic conditions but is an occurrence which should be of importance in aqueous-alcoholic systems.²⁶⁻²⁸ Nevertheless, the $\eta^1\text{-CO}_2$ complex, $\text{W}(\text{CO})_5\text{CO}_2^{2-}$, has been identified in solution from the reaction of $\text{W}(\text{CO})_6^{2-}$ and carbon dioxide, a process analogous to other reported reactions involving CO_2 and metal carbonyl anions.²⁹

As we have previously communicated, metal pentacarbonyl hydride anions of the group 6B metals react easily with carbon dioxide and carbon disulfide,¹¹ as well as with carbonyl sulfide.³⁰ All of the reactions are practically instantaneous at room temperature, affording quantitatively the corresponding pentacarbonylmetal formate, dithioformate,³¹ or monothioformate³¹ anions, respectively. Identical pentacarbonylmetal formate anions were obtained from the reaction of the corresponding metal pentacarbonyl halogen anions with thallium formate.^{32,33}

(24) We acknowledge this suggestion as being that of one of our reviewers.

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(31) Anal. Calcd for $[\text{PPN}][\text{Cr}(\text{CO})_5\text{SCHS}]$: C, 62.45; H, 3.87; S, 7.94. Found: C, 61.30; H, 4.38; S, 7.35. Anal. Calcd for $[\text{PPN}][\text{Cr}(\text{CO})_5\text{SCHO}]$: C, 63.72; H, 3.95; S, 4.05. Found: C, 63.66; H, 4.11; S, 4.13.

(32) Anal. Calcd for $[\text{PPN}][\text{W}(\text{CO})_5\text{OCHO}]$: C, 55.59; H, 3.44. Found: C, 55.77; H, 3.51.

(20) These species may be related to those previously reported by Hieber and co-workers.¹² Presently we have a program, in collaboration with Professor T. J. McNeese of Loyola College (Baltimore, MD), designed to fully characterize these reaction products.

(21) Darensbourg, M. Y.; Jimenez, P.; Sackett, J. R. *J. Organomet. Chem.* **1980**, *202*, C68.

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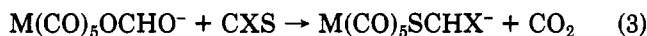
(23) Analogous CMR spectral data for the more stable alkoxide anion, $\text{W}(\text{CO})_5\text{COOMe}^-$, reveal carbon resonances at 205.7 ppm ($\delta(\text{C}_{\text{ax}})$) and 201.5 ppm ($\delta(\text{C}_{\text{eq}})$) in CD_3CN . The most intense $\nu(\text{CO})$ infrared band in the above-mentioned alkoxide adduct of tungsten occurs at 1905 cm^{-1} in CH_3CN . Unpublished data of A. Rokicki and M. Y. Darensbourg.

Table III. Refined Atomic Coordinates in Crystalline $(\text{Cr}(\text{CO})_5(\text{OSCH}))(\text{NPn}_2(\text{C}_6\text{H}_5)_6)^a$

atom ^b	x	y	z	atom ^b	x	y	z
Anion							
Cr	0.01654 (5)	-0.16708 (4)	0.25270 (4)	C(1)	-0.16422 (30)	-0.21337 (24)	0.16547 (25)
S	0.00979 (8)	-0.35772 (7)	0.14808 (7)	C(2)	0.00305 (35)	-0.22106 (28)	0.34860 (27)
O(1)	-0.27460 (22)	-0.23791 (20)	0.11381 (21)	C(3)	0.20092 (33)	-0.12623 (30)	0.33837 (29)
O(2)	-0.01022 (33)	-0.25008 (26)	0.40702 (24)	C(4)	0.01472 (32)	-0.11707 (29)	0.14774 (29)
O(3)	0.30961 (26)	-0.10134 (30)	0.38995 (27)	C(5)	0.02859 (29)	-0.02269 (26)	0.33567 (24)
O(4)	0.00477 (30)	-0.08689 (28)	0.08289 (26)	C	0.10962 (34)	-0.33933 (29)	0.10413 (31)
O(5)	0.03710 (23)	0.06778 (19)	0.38857 (19)	H ^c	0.1071 (35)	-0.4181 (32)	0.0527 (30)
O	0.17626 (28)	-0.25018 (23)	0.12046 (27)				
Cation							
P(1)	0.47953 (6)	0.11141 (6)	0.22969 (5)	C(2A1)	0.64201 (25)	0.37855 (22)	0.18570 (21)
P(2)	0.61085 (6)	0.35145 (6)	0.28012 (5)	C(2A2)	0.62468 (35)	0.47414 (28)	0.16289 (30)
N	0.58441 (22)	0.21895 (19)	0.25524 (19)	C(2A3)	0.65341 (40)	0.49441 (34)	0.09227 (36)
C(1A1)	0.56060 (25)	0.01317 (23)	0.27132 (20)	C(2A4)	0.69928 (39)	0.42190 (39)	0.04572 (33)
C(1A2)	0.48879 (30)	-0.09944 (27)	0.23777 (26)	C(2A5)	0.71524 (35)	0.32870 (34)	0.06628 (29)
C(1A3)	0.55171 (38)	-0.17395 (29)	0.27063 (30)	C(2A6)	0.68700 (28)	0.30620 (25)	0.13627 (24)
C(1A4)	0.68383 (36)	-0.13712 (31)	0.33628 (28)	C(2B1)	0.48037 (26)	0.40293 (25)	0.26546 (23)
C(1A5)	0.75508 (30)	-0.02582 (31)	0.37074 (26)	C(2B2)	0.36845 (31)	0.36231 (32)	0.15891 (26)
C(1A6)	0.69373 (27)	0.04995 (26)	0.33808 (23)	C(2B3)	0.26512 (36)	0.39769 (40)	0.14375 (32)
C(1B1)	0.35187 (25)	0.03495 (22)	0.08388 (20)	C(2B4)	0.27213 (38)	0.47251 (41)	0.23403 (37)
C(1B2)	0.37047 (30)	0.05234 (24)	0.00743 (23)	C(2B5)	0.38085 (40)	0.51236 (38)	0.33898 (34)
C(1B3)	0.27230 (37)	-0.00881 (28)	-0.10551 (24)	C(2B6)	0.48645 (31)	0.47806 (30)	0.35600 (26)
C(1B4)	0.15887 (35)	-0.08546 (29)	-0.13999 (25)	C(2C1)	0.75138 (25)	0.44029 (24)	0.41946 (21)
C(1B5)	0.14025 (31)	-0.10345 (31)	-0.06512 (27)	C(2C2)	0.82919 (31)	0.54736 (28)	0.44761 (26)
C(1B6)	0.23592 (28)	-0.04388 (28)	0.04752 (24)	C(2C3)	0.93320 (34)	0.61558 (33)	0.55562 (30)
C(1C1)	0.40524 (26)	0.14690 (24)	0.30377 (22)	C(2C4)	0.96139 (32)	0.57767 (35)	0.63550 (28)
C(1C2)	0.29758 (31)	0.18000 (32)	0.26289 (28)	C(2C5)	0.88691 (34)	0.47099 (34)	0.60915 (26)
C(1C3)	0.25056 (35)	0.21629 (35)	0.32751 (35)	C(2C6)	0.78100 (30)	0.40142 (28)	0.50050 (25)
C(1C4)	0.30872 (41)	0.21755 (35)	0.42996 (34)				
C(1C5)	0.41527 (44)	0.18513 (37)	0.47090 (31)				
C(1C6)	0.46364 (35)	0.14932 (31)	0.40785 (27)				

^a The numbers in parentheses are the estimated standard deviations in the last significant digit. ^b Atoms are labeled in agreement with Figure 1. ^c The final value of the least-squares refined isotropic thermal parameter, B , for this hydrogen atom is $8.3(10) \text{ \AA}^2$.

The metal pentacarbonyl formate anions were found to undergo exchange reactions with carbonyl sulfide and carbon disulfide to yield the corresponding metal pentacarbonyl monothioformate and dithioformate anions according to eq 3. This exchange reaction is much slower



than insertion of CXS into the metal hydride species. In the case of the chromium derivative, the exchange reaction goes to completion in several hours at room temperature, while the Mo and W analogues require a few days under similar reaction conditions. The spectral data ($\nu(\text{CO})$ and ^{13}C NMR) for the formate derivatives of metal pentacarbonyl anions of group 6B obtained in this study are summarized in Table II. All the compounds prepared exhibit the same characteristic pattern in the carbonyl stretching region of the infrared spectrum, namely, weak, weak, strong, and medium absorption bands.³⁴ This pattern is consistent with the anticipated C_{4v} symmetry of the pentacarbonylmetal formate molecules that predicts three allowed bands in the carbonyl region of the IR spectra of these species ($2A_1 + E$), along with some activity of the forbidden B_1 band. Furthermore, the infrared spectra in the $\nu(\text{CO}_2^-)$ region are congruous with those of other monodentate formate species,³⁵ consisting of a strong

antisymmetric $\nu(\text{CO}_2)$ vibration at $\sim 1610 \text{ cm}^{-1}$ and a somewhat weaker symmetrical $\nu(\text{CO}_2)$ at $\sim 1315 \text{ cm}^{-1}$. In unidentate complexes the separation between the two $\nu(\text{CO}_2)$ vibrations is larger than that in the free formate ion, where $\Delta\nu(\text{CO}_2) = 200 \text{ cm}^{-1}$.³⁶ Cotton-Kraihanzel³⁷ force constants (Table II) for the axial CO ligand (k_1) were found to increase in order of substituents as follows: formate < monothioformate < thioformate. On the other hand, the force constants for the equatorial CO ligands (k_2) remained rather constant regardless of substituent changes.

Because of the deficiency of detailed structural information on low-valent metal centers containing the formate ligand, we have subjected one of these species, namely, $[\text{PPN}][\text{Cr}(\text{CO})_5\text{SC}(\text{O})\text{H}]$, to a X-ray structure analysis.³⁸ This specific derivative was singled out for more complete scrutiny since it offered the option of either the S or O atom of the thioformate ligand being bound to the metal center. The final atomic coordinates for all non-hydrogen atoms of both the cation and anion are provided in Table III. The calculated atomic coordinates for the cation's hydrogen atoms in crystalline $[\text{PPN}][\text{Cr}(\text{CO})_5\text{SC}(\text{O})\text{H}]$ are available as supplementary material. Figure 1 presents a perspective view of the anion structure and defines the atomic numbering scheme employed. In Table IV is given bond distances and angles for all atoms in the anion $\text{Cr}(\text{CO})_5\text{SC}(\text{O})\text{H}^-$. The $[\text{PPN}]^+$ counterion was found as a well-behaved group and contained dimensions which are

(33) Doyle, G. J. *Organomet. Chem.* 1975, 84, 323.

(34) A similar pattern in the carbonyl region of the infrared spectra of products resulting from insertion of PhNCX ($X = \text{O}, \text{S}$) into $\text{M}(\text{CO})_5\text{H}^-$ is noted, e.g.: $\text{W}(\text{CO})_5\text{SCHNPh}^-$, 2060 (w), 1965 (w), 1917 (s), 1863 (m); $\text{W}(\text{CO})_5\text{OCHNPh}^-$, 2060 (w), 1963 (w), 1912 (s), 1845 (m) as $[\text{K-kryptofix-222}]^+$ salts in CH_3CN .

(35) Darenbourg, D. J.; Fischer, M. B.; Schmidt, R. E., Jr.; Baldwin, B. J. *J. Am. Chem. Soc.* 1981, 103, 1297.

(36) See, e.g.: Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds", 3rd ed.; Wiley-Interscience: New York, 1977.

(37) Cotton, F. A.; Kraihanzel, C. S. *J. Am. Chem. Soc.* 1962, 84, 4432.

(38) A preliminary account of this structural investigation can be found in ref 30.

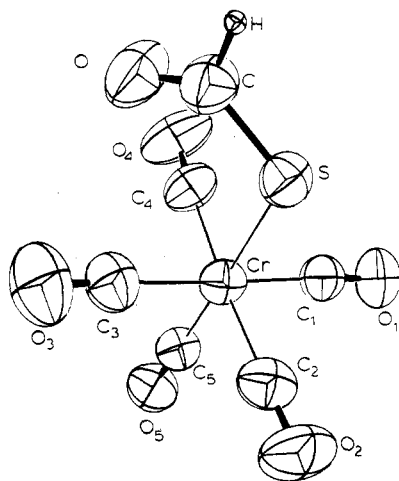


Figure 1. Perspective ORTEP drawing of the $\text{Cr(CO)}_5\text{SCHO}^-$ anion. All non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density. The lone hydrogen atom is represented by an arbitrarily small sphere which is in no way representative of its true thermal motion.

expected for it.^{39,40} The average P–N bond length is 1.582 (3) Å and the P–N–P angle is 140.1 (2)°; a complete listing of bond distances and angles may be found in the supplementary material.

As is depicted in Figure 1, the mode of binding of the thioformate ligand to the soft Cr(CO)_5 moiety is in a monodentate fashion through the sulfur atom. The disposition of the ligands about the chromium atom is that of a regular octahedron, where the average C(ax)–Cr–C(eq) angle is 90.7°. The Cr–C(eq) distances average 1.894 (4) Å, while the axial Cr–C(5) bond length is considerably shorter at 1.837 (4) Å. Hence, the monothioformate ligand, situated 2.447 (1) Å from the chromium metal center, exerts a significant trans effect. This difference in axial vs. equatorial metal–carbon bond lengths (0.057 Å) is reflected in the C–K force constants and is akin to that exhibited in complexes containing other σ -donor ligands, e.g., $\text{Cr(CO)}_5\text{O}_2\text{CCF}_3$ ⁴¹ and $\text{Cr(CO)}_5\text{SPIMe}_3$,⁴² and is seen as well in the solution reactivity of these species (vide infra). The thioformate ligand resides with its oxygen atom directly above the C(3)–Cr–C(4) quadrant and defines a plane that is almost perpendicular to and bisects the C(3)–Cr–C(4) angular arrangement. A similar orientation of the acetato ligand in the group 6B (acetato)pentacarbonylmetalates has been reported.^{41,43}

The proton NMR spectra of the pentacarbonylmetal formate derivatives show a progressive downfield shift of the formate proton absorption in order to substituents: CHO_2 , $\delta(\text{CH}) \sim 8.0 < \text{SCHO}$, $\delta(\text{CH}) \sim 10.5 < \text{CHS}_2$, $\delta(\text{CH}) \sim 11.8$. This downfield shift of the formate's proton absorption upon replacing oxygen with sulfur atoms closely resembles the situation among *N*-alkyl- and *N*-arylthioformamide anions, where the resonance positions for the thioformamide ligands are approximately midway between those of the dithioformate and formamidinate ligands.⁴⁴ As is further noted in Table II, the proton resonance of

Table IV. Anionic Bond Lengths, Polyhedral Edge Lengths (Å), and Bond Angles (Deg) in $(\text{Cr(CO)}_5(\text{OSCH}))(\text{NP}_2(\text{C}_6\text{H}_5)_6)^{a,b}$

Bond Lengths			
Cr–S	2.447 (1)	S...C(1)	3.119 (4)
		S...C(2)	3.088 (4)
Cr–C(1)	1.875 (4)	S...C(3)	3.006 (4)
Cr–C(2)	1.879 (4)	S...C(4)	3.094 (4)
Cr–C(3)	1.919 (4)		
Cr–C(4)	1.903 (4)	C(1)...C(2)	2.598 (5)
Cr–C(5)	1.837 (4)	C(1)...C(4)	2.615 (6)
		C(1)...C(5)	2.644 (5)
S–C	1.725 (5)	C(2)...C(3)	2.741 (7)
		C(2)...C(5)	2.614 (5)
O–C	1.206 (6)	C(3)...C(4)	2.759 (5)
		C(3)...C(5)	2.693 (6)
O(1)–C(1)	1.148 (5)		
O(2)–C(2)	1.146 (5)	C–H	1.06 (4)
O(3)–C(3)	1.130 (6)		
O(4)–C(4)	1.134 (5)		
O(5)–C(5)	1.151 (4)		
Bond Angles			
SCrC(1)	91.4 (1)	CrSC	109.1 (2)
SCrC(2)	90.1 (1)		
SCrC(3)	86.1 (1)	SCO	128.7 (4)
SCrC(4)	89.8 (1)	SCH	114 (2)
SCrC(5)	177.6 (1)	OCH	117 (2)
C(1)CrC(2)	87.6 (2)	CrC(1)O(1)	177.7 (3)
C(1)CrC(3)	177.6 (2)	CrC(2)O(2)	175.7 (4)
C(1)CrC(4)	87.6 (2)	CrC(3)O(3)	179.2 (4)
C(1)CrC(5)	90.9 (2)	CrC(4)O(4)	174.9 (4)
C(2)CrC(3)	92.4 (2)	CrC(5)O(5)	179.4 (3)
C(2)CrC(4)	175.2 (2)		
C(2)CrC(5)	89.4 (2)		
C(3)CrC(4)	92.4 (2)		
C(3)CrC(5)	91.6 (2)		
C(4)CrC(5)	90.9 (2)		

^a The numbers in parentheses are the estimated standard deviations in the last significant digit. ^b Atoms are labeled in agreement with Figure 1.

the formate ligands do not vary significantly with the nature of the metal center.

The carbon-13 NMR spectra of the anions show two signals due to the CO ligands and one due to the carboxylic group. In all instances the signal due to the axial carbonyl carbon was shifted downfield from the equatorial one. Both signals exhibit upfield shifts of approximately the same magnitude upon proceeding down the periodic table. The position of the carboxylic carbon signal strongly depends on the substituent itself and shifts downfield while going from formate to thioformate. This downfield chemical shift of the carboxylic carbon upon substitution of oxygen by sulfur agrees well with the values calculated from eq 4.⁴⁵ For example, $\delta_{\text{C=O}}$ observed at 167.3 ppm

$$\delta(\text{C}=\text{S}) = 1.45\delta(\text{C}=\text{O}) - 46.5 \text{ ppm} \quad (4)$$

in $\text{Cr(CO)}_5\text{OC(O)H}^-$ affords a calculated $\delta(\text{C}=\text{S})$ value of 196.1 ppm in $\text{Cr(CO)}_5\text{SC(O)H}^-$ which compares favorably with its observed value of 198.8 ppm. This in turn suggests a partial double bond between carbon and sulfur in the thioformate substituent even though the ligand binds to the metal through sulfur. In fact, the C–S bond length noted in the $\text{Cr(CO)}_5\text{SC(O)H}^-$ anion of 1.725 (5) Å is quite close to that established for partial C–S double-bond character, e.g., as in heterocyclic species of the type $\text{C}_4\text{H}_4\text{S}$ where the C–S bond distance is 1.73 Å.⁴⁶ The C–S single

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(42) Baker, E. N.; Reay, B. R. *J. Chem. Soc., Dalton Trans.* **1973**, 2205.

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(46) "Handbook of Chemistry and Physics", 53rd ed.; CRC Press: Cleveland, OH, 1972; p F-180.

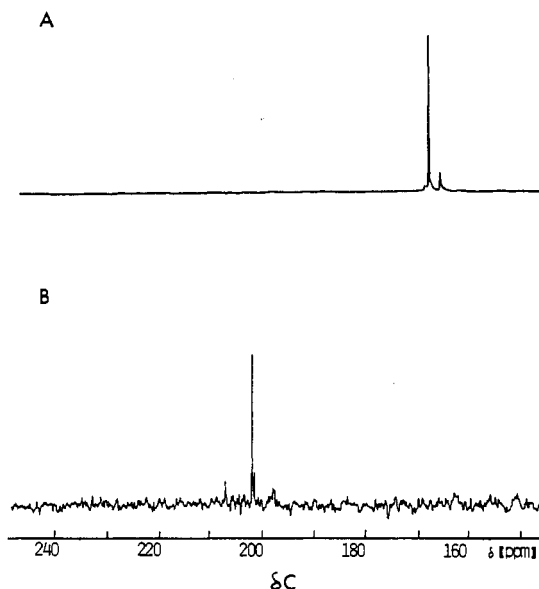


Figure 2. ^{13}C NMR spectra of $\text{W}(\text{CO})_5\text{O}_2\text{CH}^-$ in CD_3CN : A, after reaction with $^{13}\text{CO}_2$; B, after reaction with ^{13}CO .

bond distance is ~ 1.81 Å. Hence, this observation is analogous to that seen in monodentate acetate ligands bound to group 6B metals where the two carboxyl carbon to oxygen bond lengths are similar, both being shorter than a single carbon-oxygen bond.^{41,43,47}

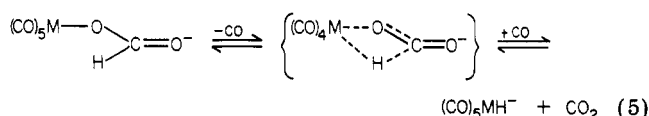
The proton-carbon coupling constants decrease in size in going from formate to thioformate, which is in agreement with the general observation that substitution on carbon by electronegative atoms increases $^1J_{\text{CH}}$ significantly.^{48a} It should be noted that this coupling constant is in the range of the coupling constant in the free formate ion in aqueous solution (194.8 Hz),^{48b} indicating that the negative charge of the metal anion resides mainly on the formate substituent. The chemical shift of the carboxylic carbon and the carbon-proton coupling constants show little dependence on the nature of the metal center.

The reaction of either the metal pentacarbonyl hydride or formate anion with carbon-13 enriched carbon dioxide give rise to metal pentacarbonyl formate anions, specifically carbon-13 enriched in the formate ligand only (Figure 2a). This labeling experiment demonstrates that no further reduction of CO_2 to CO occurs during the CO_2 insertion process since none of the label appears in the CO ligands. Analogous results were obtained when $^{13}\text{CS}_2$ was used in place of $^{13}\text{CO}_2$ in the insertion reaction. Conversely, no ^{13}C label from ^{13}CO was observed in the formate ligand during carbon monoxide exchange reactions of the pentacarbonyl formate anions (Figure 2b). The CO exchange reaction was found to decrease while going down the periodic table.⁴⁹ For derivatives of chromium, the CO exchange rate was found to depend on the formate ligand and decreased in the order $\text{OCHO} \approx \text{SCHO} \gg \text{SCHS}$.⁵⁰ This latter observation is suggestive of assistance by the uncoordinated oxygen atom of the OCHO and SCHO lig-

ands in CO dissociation, i.e., intramolecular nucleophilic addition of the distal oxygen atom of the formate to a carbonyl carbon atom. Indeed this result is consistent with the solid-state structure of these type species, where the formate's distal oxygen is in position to interact at an adjacent carbonyl site.^{35,41,43}

In support of the above contention, the CO exchange reaction in $\text{W}(\text{CO})_5\text{OCHO}^-$ has been found to proceed stereoselectively at cis positions.^{51,52} During the early stages of ^{13}CO incorporation into the $\text{W}(\text{CO})_5\text{OCHO}^-$ anion at ambient temperature in CDCl_3 , the ^{13}C resonance for the cis CO ligands at 200.2 ppm accounted for all the ^{13}CO uptake.⁵³ The ^{13}C NMR spectrum was measured at low temperature (-50°C) to avoid subsequent processes leading to CO rearrangement in the ^{13}C -enriched $\text{W}(\text{CO})_5\text{OCHO}^-$ sample during the acquisition of the NMR data.

The pentacarbonyl formate anions of the group 6B metals undergo decarboxylation processes, i.e., reaction 2 run in the reverse direction or as is more intimately described in eq 5. This process is relatively rapid for the



chromium derivative at ambient temperature, while the Mo and W formate analogues are rather inert toward CO_2 extrusion under these circumstances. Comparative decarboxylation experiments carried out in both nitrogen and carbon monoxide readily reveal that this process is inhibited in a carbon monoxide environment. The most intense $\nu(\text{CO})$ band of the $\text{Cr}(\text{CO})_5\text{H}^-$ anion grows in with time for the reaction carried out in a N_2 atmosphere with a concomitant decrease in $\nu(\text{CO})$ bands assignable to the parent $\text{Cr}(\text{CO})_5\text{O}_2\text{CH}^-$ species. In contrast for the same process carried out in a carbon monoxide atmosphere, the intensity of the $\nu(\text{CO})$ absorptions of $\text{Cr}(\text{CO})_5\text{O}_2\text{CH}^-$ are unaffected. Similar CO inhibition was noted in decarboxylation experiments involving $\text{W}(\text{CO})_5\text{O}_2\text{CH}^-$ run at a higher temperature of 60°C . Under these circumstances the primary product of decarboxylation, $\text{W}(\text{CO})_5\text{H}^-$, was not observed. Instead the hydride containing complex seen was $\text{H}[\text{W}(\text{CO})_5]_2^-$.

Hence these results indicate that metal-CO bond lability appears to be a requisite step in the intimate mechanism of C-H bond rupture or formation involving the formate ligand in the systems studied herein comprising coordinatively saturated metal centers (eq 5). Compatible with this important mechanistic aspect of CO_2 insertion and deinsertion, the rates of CO dissociation as evidenced by ^{13}CO exchange studies in both $\text{Cr}(\text{CO})_5\text{H}^-$ and $\text{Cr}(\text{CO})_5\text{O}_2\text{CH}^-$ are rapid enough to account for the corresponding rates of carboxylation and decarboxylation.⁵⁴ In the tungsten analogues although CO dissociation in $\text{W}(\text{CO})_5\text{O}_2\text{CH}^-$ is clearly faster than CO_2 extrusion, CO_2 insertion into $\text{W}(\text{CO})_5\text{H}^-$ is more facile than CO exchange in this anionic hydrido species.⁵⁵ This latter observation requires

(47) Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. *Inorg. Chem.* 1981, 20, 1287.

(48) Levy, G. C.; Lichter, R. L.; Nelson, G. L. "Carbon-13 Nuclear Magnetic Resonance Spectroscopy", 2nd ed.; Wiley-Interscience: New York, 1980: (a) p 34; (b) p 30.

(49) The carbon monoxide ligands are quite labile in both $\text{Cr}(\text{CO})_5\text{OCHO}^-$ and $\text{Mo}(\text{CO})_5\text{OCHO}^-$, where 92 and 82% CO exchange with ^{13}CO in solution (20 kPa) is observed after only 30 min at ambient temperature. On the other hand, only 10% enrichment of $\text{W}(\text{CO})_5\text{OCHO}^-$ was observed under the same conditions.

(50) The corresponding levels of enrichment after 30 min at ambient temperature are as follows: 92, 90, and 3%, respectively.

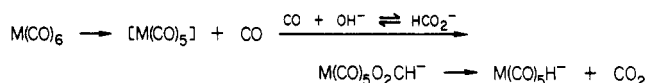
(51) In addition to the assistance of CO dissociation by the free carboxylic oxygen atom, the formate ligand bound to d^6 metal pentacarbonyls probably represents another example of a cis-labilizing ligand based on the arguments of Atwood and Brown.⁵²

(52) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* 1976, 98, 3160.

(53) A similar observation was reported for the $\text{W}(\text{CO})_5\text{O}_2\text{CCH}_3^-$ anionic species.⁴³

(54) Since all of these carboxylation reactions occur rapidly as seen by means of conventional rate studies, it is not possible to discern any discrepancy in these key mechanistic steps. More refined rate studies are planned employing FT infrared spectroscopy.

Scheme III



as well as comparative rates of R^- addition to the CO ligands in iron and group 6B carbonyls.⁶³

These results do not however preclude the presence of $\text{M(CO)}_5\text{O}_2\text{CH}^-$ species during catalysis of the WGS, for there are several facile routes for their formation once catalysis has ensued which do not require dissociation of CO from M(CO)_6 .¹¹ For example, the $[\text{M(CO)}_5]$ intermediate afforded upon reductive elimination of hydrogen from $\text{M(CO)}_5\text{H}_2$ is probably scavenged as effectively by HCO_2^- as by CO, since these pentacoordinate transients are rather indiscriminate in their reactivity toward incoming ligands.⁶⁴⁻⁶⁶ Of course reaction 2 (i.e., $\text{M-H}^- + \text{CO}_2 \rightleftharpoons \text{MO}_2\text{CH}^-$) provides an easy pathway to metalloformate derivatives. In addition, we have some preliminary results in aprotic solvents which suggest that crypt-222 solubilized KHCO_2 assists CO loss in M(CO)_6 with concomitant formation of $\text{M(CO)}_5\text{O}_2\text{CH}^-$.⁶⁷ However, this process is extremely slow relative to hydroxide addition to M(CO)_6 and possibly involves an intermediate of the type proposed for the addition of the isoelectronic nucleophile NO_2^- to the carbon center in metal carbonyls.⁶⁸

In summary it is our contention that the premier mechanistic step in the thermal catalysis of the WGS by

group 6B metal carbonyls entails activation of carbon monoxide by the transition metal toward nucleophilic attack by hydroxide ions and not by Scheme III as has been suggested by others.⁵⁹⁻⁶¹ Indeed activation parameters determined as a function of the metal⁵⁹ are inconsistent with such a proposal. On the other hand, photolysis of M(CO)_6 in the presence of HCO_2^- can bias the process in favor of a simple formate ion decomposition mechanism as described in Scheme III.⁵⁹⁻⁶¹

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Registry No. [K-kryptofix-222]⁺[HCr(CO)₅]⁻, 82880-51-1; [K-kryptofix-222]⁺[HMo(CO)₅]⁻, 82880-52-2; [K-kryptofix-222]⁺[HW(CO)₅]⁻, 82880-53-3; [K-kryptofix-222]⁺[Cr(CO)₅OCHO]⁻, 82880-54-4; [K-kryptofix-222]⁺[Mo(CO)₅OCHO]⁻, 82880-55-5; [K-kryptofix-222]⁺[W(CO)₅OCHO]⁻, 82880-56-6; [Cr(CO)₅OCHO]⁻PPN⁺, 82880-57-7; [Mo(CO)₅OCHO]⁻PPN⁺, 82880-58-8; [W(CO)₅OCHO]⁻PPN⁺, 36499-81-7; [K-kryptofix-222]⁺[Cr(CO)₅SCHO]⁻, 82880-59-9; [K-kryptofix-222]⁺[Mo(CO)₅SCHO]⁻, 82880-61-3; [K-kryptofix-222]⁺[W(CO)₅SCHO]⁻, 82880-63-5; [Cr(CO)₅SCHO]⁻PPN⁺, 80215-86-7; [W(CO)₅SCHO]⁻PPN⁺, 82880-64-6; [K-kryptofix-222]⁺[Cr(CO)₅SCHS]⁻, 82880-65-7; [K-kryptofix-222]⁺[Mo(CO)₅SCHS]⁻, 82880-66-8; [K-kryptofix-222]⁺[W(CO)₅SCHS]⁻, 82880-67-9; [Cr(CO)₅SCHS]⁻PPN⁺, 82880-68-0; [Mo(CO)₅SCHS]⁻PPN⁺, 82880-69-1; [W(CO)₅SCHS]⁻PPN⁺, 82880-70-4; Cr(CO)₆, 13007-92-6; Mo(CO)₆, 13939-06-5; W(CO)₆, 14040-11-0; CO₂, 124-38-9; COS, 463-58-1; CS₂, 75-15-0; ¹³CO, 1641-69-6; H₂O, 7732-18-5; [K-kryptofix-222][OH], 50648-41-4.

Supplementary Material Available: Lists of structure factor amplitudes, table of anisotropic thermal parameters for all non-hydrogen atoms, tables of hydrogen atom positions and bond lengths and angles in the cation, and ORTEP drawing of cation PPN (33 pages). Ordering information is given on any current masthead page.

(63) Darensbourg, M. Y.; Conder, H. L.; Darensbourg, D. J.; Hasday, C. J. *Am. Chem. Soc.* 1973, 95, 5919.

(64) Hyde, C. L.; Darensbourg, D. J. *Inorg. Chem.* 1973, 12, 1286.

(65) Covey, W. D.; Brown, T. L. *Inorg. Chem.* 1973, 12, 2820.

(66) Dobson, G. R. *Inorg. Chem.* 1980, 19, 1415.

(67) For example, M(CO)_6 (M = Cr, W) in the presence of crypt-222 solubilized KHCO_2 in CH_3CN at 47 °C exhibits infrared bands assignable to the corresponding $\text{M(CO)}_5\text{O}_2\text{CH}^-$ species (~5% conversion) after 24 h.

(68) Stevens, R. E.; Yanta, T. J.; Gladfelter, W. L. *J. Am. Chem. Soc.* 1981, 103, 4981.

Reactions of Formic Acid. 1. The Iridium-Catalyzed Synthesis of Acetic Acid from Methyl Formate[†]

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A very efficient and simple process for "isomerizing" methyl formate to acetic acid utilized a soluble iridium catalyst, promoted by methyl iodide, and was conducted in a carboxylic acid solvent. The acid solvent was found to be necessary and in the simplest case was the product acetic acid. The reaction proceeded in the carboxylic acid by transesterification as a first step, followed by reaction of the formic acid formed in this manner. The rate of formation of acetic acid was a direct function of formic acid, was first order in iridium, and was a positive function of the iodide concentration at lower levels. Water retarded or completely inhibited acetic acid formation and allowed an alternate pathway by which methane and carbon dioxide were the principal products. A mechanism is proposed which involves a unique iridium(III) complex containing hydride, iodide, carbon dioxide, and a methyl group as ligands. Migration of the methyl group to the carbon of the ligated carbon dioxide is the source of acetate. Formaldehyde reacted in this system by first condensing to methyl formate in an iridium-catalyzed Tischenko reaction. This was followed by "isomerization" to acetic acid.

Introduction

Formic acid and methyl formate are simple, versatile products of CO/H₂ chemistry. They are unique in that they contain a C-H bond that is aldehyde-like, yet dif-

ferent due to the influence of the C-OH(R) bond. Formic acid is a byproduct of butane oxidation to acetic acid or can be made by the hydrolysis of methyl formate.¹ Methyl

[†] Dedicated to the memory of the late Rowland Pettit.

(1) (a) Czaikowski, M. P.; Bayne, A. R. *Hydrocarbon Process.* 1980, 59, 103. (b) Leonard, J. D. U.S. Patent 4 299 981, 1981.