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Alternate Synthetic Routes to the Mononuclear Pentacarbonyl Hydrides of Cr, Mo, and W

Marcetta Y. Darensbourg* and Sydney Slater

Department of Chemistry, Tulane University
New Orleans, Louisiana 70118

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Despite the simplicity of the hydridocarbonylates $HM(CO)_5^-$ (M = Cr, Mo, W), until recently[1] a complete characterization of even one of them was not available. Attempts to develop a general synthesis of $HM(CO)_5^-$ via protonation of $M(CO)_5^{2-}$ according to the original method of Behrens[2] as effected for $HCr(CO)_5^-$ were thwarted by the lack of a convenient, safe synthesis of $M(CO)_5^{2-}$. While $Cr(CO)_5^{2-}$ can be obtained relatively pure by Na^0/liquid NH_3 reduction,[2] other group 6A $M(CO)_5^{2-}$ are obtained as mixtures of $M_2(CO)_{10}^{2-}$ and $M(CO)_5^{2-}$ or as solutions of $Na(HMPA)_x{}^+M(CO)_5^{2-}$ from which isolation is difficult.[3]

To be circumvented in synthetic routes to $HM(CO)_5^-$ are a variety of reaction modes which lead to the very stable bridging hydrides μ-$HM_2(CO)_{10}^-$ (eq 1–3).

$$2M(CO)_5^{2-} \xrightarrow{[O]} M_2(CO)_{10}^{2-} \xrightarrow{H^+} \mu\text{-}HM_2(CO)_{10}^- \quad (1)$$

$$HM(CO)_5^- \xrightarrow{[O]\text{ or }H^+} \mu\text{-}HM_2(CO)_{10}^- \quad (2)$$

$$HM(CO)_5^- + M(CO)_5L \rightarrow \mu\text{-}HM_2(CO)_{10}^- \quad (3)$$

$$L = \text{labile ligand}$$

Our earlier report of the synthesis of Et_4N^+ or Ph_4As^+ salts of $HCr(CO)_5^-$ by the methanolic protonation of $Cr(CO)_5^{2-}$ generated by Na^0/liquid NH_3 reduction stands as a good synthetic procedure.[1] However, the following method, described for W specifically and utilizing Cooper's method[4] for generating clean $M(CO)_5^{2-}$, is general for Cr and Mo also. Using rigorously O_2-free conditions a 60-mL solution of 3.0 g $W(CO)_5(NMe_3)$ in THF was cooled to −78 °C and 0.2 M sodium naphthalenide in THF added dropwise until the color of the stirred solution maintained a dark green, indicating a slight excess of Na(naph). To the cold reaction solution was added 20 mL of a methanol solution containing 4.5 g of PPN^+Cl^- ($PPN^+ = Ph_3P\text{-}N\text{-}PPh_3{}^+$). After warming to 22 °C, the solvent mixture was removed in vacuo. The residue was taken up in 40 mL of THF followed by addition of 40 mL of dry Et_2O to precipitate excess PPN^+Cl^-. The solution was filtered through Celite and concentrated to ca. 20 mL. Hexane (60 mL) was added producing a yellow precipitate which was isolated by cannulation of the mother liquor from the precipitate, yield 3.0 g (70%). The $PPN^+HW(CO)_5^-$ was recrystallized from THF/hexane. A similar procedure was used to obtain $PPh_4{}^+HW(CO)_5^-$. Anal. Calcd for $PPh_4{}^+HW(CO)_5^-$: C, 52.41; H, 3.16; P, 4.67. Found: C, 52.04; H, 3.28; P, 4.66. Chromium and molybdenum derivatives were also obtained analytically pure by this method. Solutions of $HMo(CO)_5^-$ salts were never allowed to exceed 0 °C; otherwise decomposition to μ-$H[Mo(CO)_5]_2^-$ occurred at a moderate rate.

Once spectrally identified it became clear that a variety of reactions may be used to produce $HM(CO)_5^-$ (eq 4–7).[5–7]

$$K\cdot crypt\ 222^+OH^- + M(CO)_6 \rightarrow [M(CO)_5C({=}O)OH^-] \rightarrow K\cdot crypt^+HM(CO)_5^- + CO_2 \quad (4)^5$$

$$M = W, Mo, Cr$$

$$Cr(CO)_5(OC({=}O)H)^- \xrightarrow{\text{decomposition}} HCr(CO)_5^- + CO_2 \quad (5)^5$$

$$HVCp(CO)_3^- + Cr(CO)_6 \rightarrow HCr(CO)_5^- + CpV(CO)_4 \quad (6)^6$$

$$LiAlH_4 + Cr(CO)_5Cl^- \rightarrow HCr(CO)_5^- + LiCl + AlH_3 \quad (7)^7$$

Table I. Spectral Properties of $[PPN^+][HM(CO)_5^-]$

M	IR,[a] $\nu(CO)$, cm^{-1} $A_1{}^2$ (vw)	E (s)	$A_1{}^1$ (m)	P NMR[b] δ(M–H) ($Me_4Si\rightarrow$)	C NMR,[b,c] $\delta(^{13}CO)$ ($\leftarrow Me_4Si$) cis	trans
Cr	2016	1884	1856	−6.92	228.7	
					227.9[d]	231.5[d]
Mo	2030	1893	1858	−4.0	215.5[e]	219.6[e]
W	2029	1889	1858	−4.2[f]	205.3	209.6

[a] THF solution, measured on a Perkin–Elmer 283B infrared spectrophotometer. [b] CD_3CN solution, Me_4Si reference, measured on a Varian EM-390 spectrometer (^1H NMR) and a JEOL FX60 (C NMR) at ambient temperatures except where noted. [c] C-13 NMR spectral measurements were provided by Dr. Andrzej Rokicki, Tulane University. [d] <0 °C. [e] Spectra measured at 0 °C in order to inhibit decomposition to μ-$H[Mo(CO)_5]_2^-$. Ambient temperature spectra show same two band positions. [f] $J_{^{183}W-H} = 53.4$ Hz.

Although the mechanistic implications of eq 4–6 are of far-reaching significance, for reasons of expense and/or time none are suitable approaches for general, medium-scale syntheses. Equation 7 involves a hydride/halide ligand exchange which yielded spectrally pure $HCr(CO)_5^-$ but in our hands presented purification problems.

Pursuing the hydride/labile ligand exchange technique a second synthesis was developed (eq 8) which is feasible for M = Cr and W.

$$M(CO)_5pip + PPN^+BH_4^- \xrightarrow{pip} [(OC)_5M\cdot\cdot H\cdot\cdot BH_3^-] \xrightarrow{pip} pip{\rightarrow}BH_3 + HM(CO)_5^- \quad (8)$$

A typical preparation follows: To the dry reactants, 1.0 g of $W(CO)_5pip$ and 1.35 g of $PPNBH_4$, was added 100 mL of THF. After stirring for 1 h at room temperature the solution was concentrated to 30 mL to which 30 mL of Et_2O was added. Following filtration the solution was concentrated and hexane added yielding a light yellow oil. Trituration with hexane yielded a yellow solid which was dried in vacuo, yield 1.6 g or 75%. The reaction has worked equally well using $W(CO)_5(NMe_3)$ as starting material.

Three major factors are crucial to the success of the latter synthesis. First, it is imperative that the reaction proceed rapidly, thus minimizing the chance of product loss via eq 3. Secondly, if CO lability of the likely intermediate of eq 8 is great, a pathway is opened for production of the stable μ_2-$H_2BH_2M(CO)_4^-$. This was the major product when this approach was used for M = Mo.[8] Thirdly, of import is the relative stabilities of the labile ligand–transition metal vs. labile ligand–borane adduct. Tetrahydrofuran as labile ligand in photochemically generated THF–$M(CO)_5$ did not effectively compete for BH_3, resulting in mixtures containing $HM(CO)_5^-$, μ_2-$H_2BH_2M(CO)_4^-$,[9,10] and μ-$HM_2(CO)_{10}^-$. Separate experiments have shown that the following reactions of BH_3 with isolated $HCr(CO)_5^-$ also yielded the bidentate borohydride and bridging hydride derivatives. The proposed monodentate borohydride complex intermediate in both eq 8 and 9 could not be isolated; however, a transient IR band at 1927 cm^{-1}, whose position as well as rate of appearance and disappearance were consistent with the formulation of a M–H–BH_3 intermediate, was observed under the reaction conditions of both eq 8 and 9 for M = Cr.

The spectral data in Table I are exceptional only in the fact that this is the first collection of such data. As noted previously[1] for $HCr(CO)_5^-$ the high frequency $\nu(CO)$ IR bands of all $HM(CO)_5^-$ anions are of extremely low intensity due to the deviation

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(1) Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644.

(2) Behrens, H.; Weber, R. *Z. Anorg. Allgem. Chem.* **1957**, *241*, 122. Behrens, H.; Vogl, J. *Ibid.* **1957**, *291*, 123. *Chem. Ber.* **1963**, *96*, 2220.

(3) Ellis, J. E.; Hagen, G. P. *J. Am. Chem. Soc.* **1974**, *96*, 7825. *Inorg. Chem.* **1977**, *16*, 1357.

(4) Cooper, N. J.; Maher, J. N.; Beatty, R. P. *J. Am. Chem. Soc.*, in press.

(5) Darensbourg, D. J.; Rokicki, A.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 3223. Darensbourg, D. J.; Rokicki, A. *ACS Symp. Ser.* **1981**, *No. 152*, 107.

(6) Jones, W. D.; Huggins, J. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1981**, *103*, 4415.

(7) Darensbourg, M. Y.; Tee, T. S., unpublished results.

(8) Kirtley, S. W.; Andrews, M. A.; Bau, R.; Grynkewich, G. W.; Marks, T. J.; Tipton, D. L.; Whittlesey, B. R. *J. Am. Chem. Soc.* **1977**, *99*, 7154.

(9) Proton and C-13 magnetic resonance spectra as well as ν(CO) and ν(B–H) IR spectra of the bidentate borohydride complex anions compared well with the Mo derivative.[8] In addition, an X-ray crystal structure analysis established the similarity of $PPN^+\mu_2$-$H_2BH_2Cr(CO)_4^-$ with the Mo analogue.[10,11]

(10) Marks, M. Ph.D. Thesis, University of Southern California, 1981.

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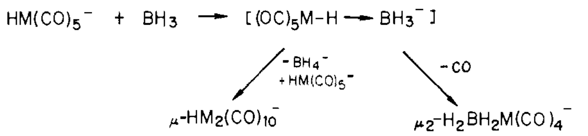

(9)

from strict octahedral symmetry (C_{trans}–Cr–C_{cis} = 95.4°).[11] As evidenced by the CMR data the $HCr(CO)_5^-$ anion shows an intramolecular CO_{cis}–CO_{trans} exchange process that is currently under investigation.[12]

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(11) A full report of the X-ray crystal structures of $HCr(CO)_5^-$ and μ_2-$H_2BH_2Cr(CO)_4^-$ and the acid/base chemistry involved in their interconversions is being prepared.

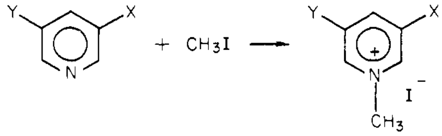
(12) Darensbourg, D. J.; Darensbourg, M. Y.; Rokicki, A.; Slater, S., manuscript in preparation.

Transition-State Variation in the Menshutkin Reaction

J. Milton Harris,* M. Steven Paley, and
Thomas W. Prasthofer

Department of Chemistry
The University of Alabama in Huntsville
Huntsville, Alabama 35899
Received May 11, 1981

The concept of a variable transition state (TS) has been of great use in explaining the properties of organic reactions, and several theoretical methods for predicting variations in TS structure have seen extensive application.[1-7] However, several groups have recently observed invariant selectivity for reactions showing large changes in reactivity.[8-11] Since this finding is most simply interpreted as indicating a constancy in TS structure, it has led to questioning of the otherwise successful methods for predicting TS variation.[9] Alternative, more convoluted, arguments can be made to retain TS variability in these cases,[1b,4a] and it is quite possible that selectivity is sometimes an insensitive probe of TS structure. The general importance of this question prompted us to apply another probe of TS structure to one of the reactions reported to give invariant selectivity. Thus we have determined kinetic α-deuterium isotope effects (α-d's) for the same series of reactants found by Arnett and Reich[8] to give invariant selectivity in the Menshutkin reaction (reaction 1).



(1)

Table I. α-Deuterium Isotope Effects for Reaction of 3-X-5-Y-Substituted Pyridines with Methyl Iodide in 2-Nitropropane at 25 °C

3-X	5-Y	rel rate	k_{CH_3I}/k_{CD_3I}
CH_3	CH_3	389	0.908 ± 0.002
CH_3	H	214	0.851 ± 0.001
H	H	138	0.850 ± 0.001
Cl	H	10.8	0.835 ± 0.002
Cl	Cl	1	0.810 ± 0.003

[a] Rate constants were determined conductimetrically as described in ref 8 and are the result of at least five runs. Error limits of the isotope effects are calculated from the standard deviations of the mean for the individual rate constants for protium and deuterium by use of the formula $s_{\alpha\text{-d}} = k_H/k_D(s_H/k_H + s_D/k_D)$ where $s_{\alpha\text{-d}}$ represents the standard deviation of the mean for the α-d, and s_H and s_D represent the standard deviations of the mean for protium and deuterium.

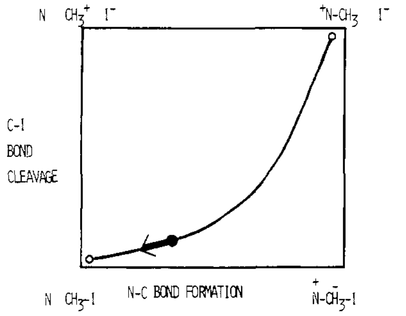


Figure 1. A potential energy diagram for a Menshutkin reaction in which N–C bond formation precedes C–I bond cleavage. Energy maxima and minima are represented by closed and open circles, respectively.

According to current interpretation, the α-d is a sensitive probe of the relative extent of crowding in the TS and in the reactant, so that a decrease in crowding results in an α-d greater than unity and an increase in crowding results in an α-d of less than unity.[12,13] Further, a gradual change in α-d is interpreted as indicating a gradual change in TS structure, and a constancy in α-d is interpreted as indicating an invariance in TS structure.[8] The α-d thus appears to be a suitable probe for investigating the proposal of an invariant TS for the Menshutkin reaction.

The results of our kinetic measurements are presented in Table I. Obviously, the α-d's do change, thus indicating variation in TS structure for this reaction, despite conclusions to the contrary based on the RSP.[8] Explanations of the failure of selectivity to vary with reactivity have been presented elsewhere and we will not detail them here.[1b,4a] Simply put, selectivity is a relatively insensitive probe and frequently does show an invariance in cases in which the TS does vary.

Current theories of TS variation can be used to explain the trend in α-d's observed for the Menshutkin reaction. The exothermicity,[8] sensitivity to steric effects ($k_{MeI} > k_{EtI}$),[8] and inverse α-d's (Table I)[14] for this reaction are consistent with an early, crowded TS in which bond making between nitrogen and carbon is more advanced than bond breaking between carbon and iodine.[15] The extent of N–C bond formation in the TS is indicated by four different probes to be about 30% of a complete N–C bond.[8,16-18] These

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(1) (a) Jencks, D. A.; Jencks, W. P. *J. Am. Chem. Soc.* **1977**, *99*, 7948. (b) Young, P. R.; Jencks, W. P. *Ibid.* **1979**, *101*, 3288.

(2) (a) Thornton, E. R. *J. Am. Chem. Soc.* **1967**, *89*, 2915. Winey, D. A.; Thornton, E. A. *Ibid.* **1975**, *97*, 3102.

(3) Gajewski, J. J.; Conrad, N. D. *J. Am. Chem. Soc.* **1979**, *101*, 6693.

(4) (a) Harris, J. M.; Shafer, S. G.; Moffatt, J. R.; Becker, A. R. *J. Am. Chem. Soc.* **1979**, *101*, 3295. (b) Shafer, S. G.; Harris, J. M., *J. Org. Chem.* **1981**, *46*, 2164.

(5) Shiner, V. J., Jr.; Seib, R. C. *J. Am. Chem. Soc.* **1976**, *98*, 862.

(6) (a) Bernasconi, C. F. *Acc. Chem. Res.* **1978**, *11*, 147. (b) Bernasconi, C. F.; Gandler, J. R. *J. Am. Chem. Soc.* **1978**, *100*, 8117.

(7) (a) Albery, W. J.; Kreevoy, M. M. *Prog. Phys. Org. Chem.* **1978**, *13*, 87. (b) Albery, W. J. "Progress in Reaction Kinetics"; Pergamon: Oxford, 1967; Vol. 4, p 355. (c) More O'Ferrall, R. A. *J. Chem. Soc. B* **1970**, 274. (d) Bunnett, J. F. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 225.

(8) Arnett, E. M.; Reich, R. *J. Am. Chem. Soc.* **1980**, *102*, 5892.

(9) Bordwell, F. G.; Hughes, D. L. *J. Org. Chem.* **1980**, *45*, 3314, 3320.

(10) Koshy, K. M.; Roy, D.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 357.

(11) (a) Pross, A. *Adv. Phys. Chem.* **1977**, *14*, 69. (b) Giese, B. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 125.

(12) Shiner, V. J., Jr. In "Isotope Effects in Chemical Reactions"; Collins, C. J., Bowman, N. S., Eds.; Van Nostrand Reinhold: New York, 1970; Chapter 2.

(13) (a) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980. (b) Knier, B. L.; Jencks, W. P. *J. Am. Chem. Soc.* **1980**, *102*, 6789.

(14) Leffek, K. T.; McLean, J. W. *Can. J. Chem.* **1965**, *43*, 40.

(15) We differ with the view of Arnett and Reich[8] that the TS for this reaction is loose with the rupture of the C–I bond being almost complete. See also: le Noble, W. J.; Miller, A. R. *J. Org. Chem.* **1979**, *44*, 889 and references cited therein.

(16) Matsui, T.; Tokura, N. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1751.

(17) Abraham, M. H.; Grellier, P. L. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1735.

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