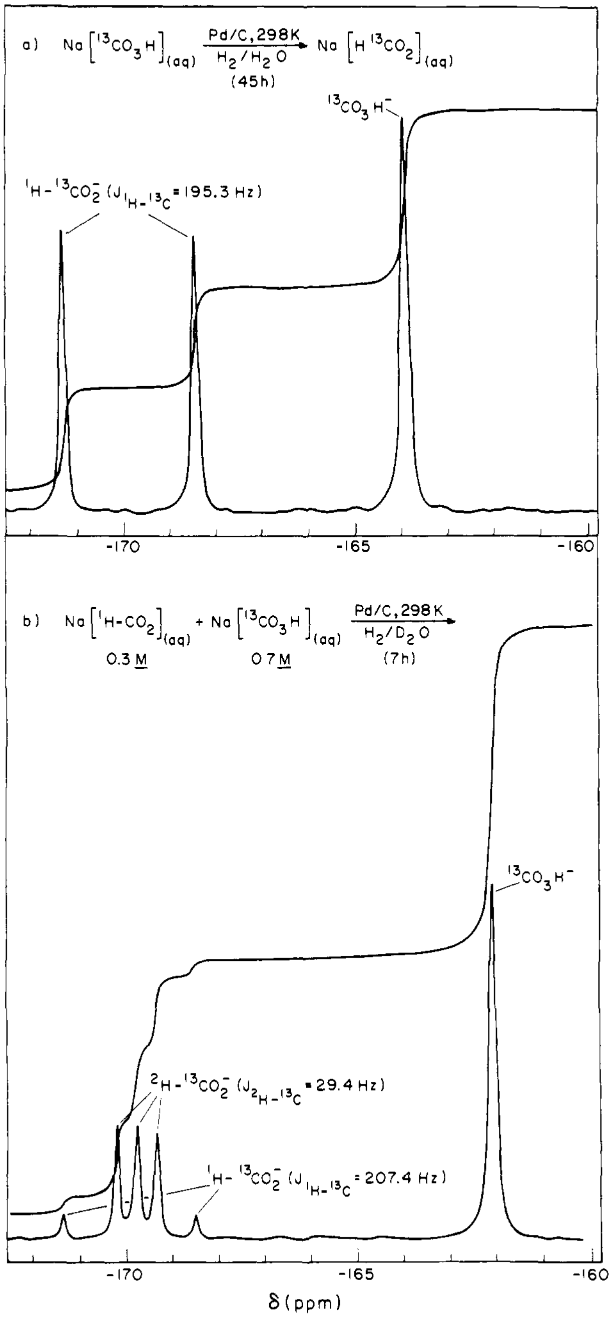

Figure 2. ^{13}C NMR spectrum of reaction mixtures: (a) solution was initially 99% ^{13}C 1.0 M $NaCO_3H$, spectrum of reaction mixture at 20-h reaction time in the presence of 1 atm H_2 at 298 K with 5% Pd/C as the catalyst; (b) initial solution was 0.3 M $NaHCO_2$ and 0.7 M $Na^{13}CO_3H$ in D_2O, spectrum is shown after 7-h exposure to catalysis conditions, 1 atm H_2, 298 K, 5% Pd/C catalysts. Chemical shifts are in ppm vs. $Si(CH_3)_4$ using a CH_3CN external standard.

kinetics can be improved to achieve useful electrochemical rates.

Acknowledgment. This research was supported in part by the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, and in part through the National Science Foundation, Materials Research Laboratory Program at the M.I.T. Center for Materials Science and Engineering. Support from the Camille and Henry Dreyfus Foundation is gratefully acknowledged. C.J.S. acknowledges support as a Postdoctoral Fellow by the Swiss National Science Foundation. We also acknowledge useful discussions with Professor Alexander M. Klibanov.

Registry No. Sodium bicarbonate, 144-55-8; sodium formate, 141-53-7; palladium, 7440-05-3.

Gas-Phase Reactions of Group 8 Metal Hydride Ions (FeD^+, CoD^+, and NiD^+) with Hydrocarbons

T. J. Carlin, L. Sallans, C. J. Cassady, D. B. Jacobson, and B. S. Freiser*

Department of Chemistry, Purdue University
West Lafayette, Indiana 47907

Received May 25, 1983

Understanding the activation of C–H and C–C bonds by transition metals continues to be one of the most challenging problems in the field of catalysis.[1] Recent gas-phase studies of the reactions of atomic metal ions with hydrocarbons represent an approach to access the inherent reactivity of these ions in the absence of solvent or ligand interferences.[2-12] A logical extension of this research is to study the effects that small ligands bound to the metal center have on the gas-phase metal ion reactivity.[2] In this paper, we report the gas phase reactions of the first-row, group 8 transition-metal hydrides with various hydrocarbons.

Metal hydrides were formed in a complex experiment[8] using a Fourier transform mass spectrometer (FTMS) equipped with a pulsed inlet valve.[9] Reaction of laser-desorbed[4-9] Fe^+ and Co^+ with nitromethane or methylnitrite and Ni^+ with methylnitrite yields a methoxy–metal moiety which decomposes by loss of formaldehyde under collisional activation[6,7] to form the corresponding metal hydride (reaction 1) in good yield.

$$M^+ + CD_3ONO \xrightarrow{-NO} MOCD_3^+ \xrightarrow{-CD_2O} MD^+ \qquad (1)$$

The major primary reactions (>5%) of FeD^+, CoD^+, and NiD^+ with H_2 and a variety of simple hydrocarbons are listed in Table I. Previously, H/D exchange reactions have been employed to indicate metal hydride character.[5] It is clear that not all hydride species will exchange, since FeD^+ does not exchange with hydrogen despite its obvious hydride character.

Only NiD^+ is observed to react with methane. Oxidative addition to the C–H bond is followed by loss of HD or CH_3D forming $NiCH_3^+$ or NiH^+, respectively. This represents a surprising change in reactivity since $D(M^+\text{–}CH_3)$ and $D(M^+\text{–}H)$ are considerably stronger for Fe^+ and Co^+ than for Ni^+;[3e] yet both of these hydrides are unreactive with methane. With ethane, which has a slightly weaker C–H bond, NiD^+ and CoD^+ both react losing HD to form a $MC_2H_5^+$ product in contrast to the bare metal ions which do not react with ethane. NiD^+ and CoD^+ react with propane to form metal–allyl products. FeD^+, however, reacts with propane forming only $FeC_3H_7^+$ by a single HD loss. All three of the metal hydrides react with *n*-butane and 2-methylpropane but with differing product distributions. None of the ions show

---

(1) Kochi, J. K. "Organometallic Mechanisms and Catalysis"; Academic Press: New York, 1978.

(2) (a) Allison, J.; Ridge, D. P. *J. Organomet. Chem.* **1979**, *99*, C11. (b) Allison, J.; Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 1332. (c) Allison, J.; Ridge, D. P. *Ibid.* **1979**, *101*, 4998. (d) Freas, R. B.; Ridge, D. P. *Ibid.* **1980**, *102*, 7131.

(3) (a) Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 784; (b) *Ibid.* **1981**, *103*, 6628. (c) Armentrout, P. B.; Halle, L. F.; Beauchamp, J. L. *Ibid.* **1981**, *103*, 6624; (d) *Ibid.* **1981**, *103*, 6501. (e) *Organometallics* **1982**, *1*, 963.

(4) Byrd, G. D.; Burnier, R. C.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 3565 and references therein.

(5) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944.

(6) Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

(7) (a) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 736; (b) *Ibid.* **1983**, *105*, 5197.

(8) Cassady, C. J.; Freiser, B. S. Presented at the 31st Annual Conference on Mass Spectrometry and Allied Topics, Boston, MA, May 12, 1983.

(9) Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

(10) Halle, L. F.; Houriet, R.; Kappes, M. M.; Staley, R. H.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1982**, *104*, 6293.

(11) Similar reactivity of $CpRhD^+$ has been observed: Beauchamp, J. L.; Stevens, A. E.; Corderman, R. R. *Pure Appl. Chem.* **1979**, *51*, 967. This result is less surprising considering the known preference of Rh^+ for C–H bond addition.

(12) Jacobson, D. B.; Freiser, B. S., unpublished results.

0002-7863/83/1505-6320$01.50/0

Table I. Percent Abundance of Products Observed in the Reactions of MD^+ Ions with Various Hydrocarbons

hydrocarbon	products	metal hydride ion		
		FeD^+	CoD^+	NiD^+
H_2	$MH^+ + HD$	NR	100	100
CH_4	$MH^+ + CH_3D$	NR	NR	20
	$MCH_3{}^+ + HD$			80
C_2H_6	$MC_2H_5{}^+ + HD$	NR	100	100
C_3H_8	$MC_3H_5{}^+ + HD, H_2$		100	100
	$MC_3H_7{}^+ + HD$	100		
n-C_4H_{10}	$MC_3H_5{}^+ + HD, CH_4$			77
	$MC_4H_7{}^+ + HD, H_2$	60	100	23
	$MC_4H_9{}^+ + HD$	40		
i-C_4H_{10}	$MC_3M_5{}^+ + HD, CH_4$			67
	$MC_4H_7{}^+ + HD, H_2$	55	100	33
	$MC_4H_9{}^+ + HD$	45		
neo-C_5H_{12}	$MC_4H_7{}^+ + HD, CH_4$	12	100	100
	$MC_5H_{11}{}^+ + HD$	88		
C_2H_4	$MH^+ + C_2H_3D$	100	77	17
	$MC_2H_3{}^+ + HD$		10	28
	$MC_2H_2D^+ + H_2$		13	55
C_3H_6	$MH^+ + C_3H_5D$	18		
	$MCH_3{}^+ + C_2H_3D$	11	6	9
	$MCH_2D^+ + C_2H_4$	6	4	4
	$MC_2H_4{}^+ + CH_2D$			9
	$MC_2H_3D^+ + CH_3$			8
	$MC_3H_5{}^+ + HD$	28	36	37
	$MC_3H_4D^+ + H_2$	37	54	33
c-C_6H_6	$MC_6H_5{}^+ + HD$			17
	$MC_6H_6{}^+ + D$	31	100	37
	$MC_6H_5D^+ + H$	52		43
	$MC_6H_6D^+$	17		3

major product differences between the two butane isomers, in contrast to the bare metals whose reactivity differs with the change in the carbon skeleton.[3] FeD^+ forms both an alkyl and allyl product, while CoD^+ forms exclusively a metal–allyl product. Once again NiD^+ is an exceptional case, losing CH_4 and HD as its major pathway. CoD^+ and NiD^+ both react with neopentane by sequential HD and CH_4 loss to form metal–allyl products exclusively. FeD^+, however, loses predominantly HD to form initially the neopentyl-iron ion. In this case multiple dehydrogenations are not observed due to the absence of β-hydrogens.

While none of the bare metal ions under consideration react with ethene, all three hydrides are reactive producing D/H exchange and (except for FeD^+) dehydrogenation products. Where dehydrogenation does occur, so does considerable scrambling of the deuterium label. Similarly, all three hydrides dehydrogenate propene as the major product with considerable retention of deuterium. Both of these results require a reversible β-hydrogen transfer in the reaction complex. Minor products corresponding to loss or retention of $CH_3\cdot$ are consistent with CID results on metal–allyl complexes formed by an alternate route.[12]

Benzene displaces D· from CoD^+ as the only product. This is consistent with collisional activation of an intact benzene–hydride complex of Co^+ which produced $Co(C_6H_6)^+$ exclusively.[12] In the case of FeD^+, loss of H· is the main product indicating that the deuterium and the ring protons exchange. NiD^+ reacts similarly to FeD^+ but also produces a dehydrogenation product suggesting a metal phenyl structure for the exchange intermediate.

These preliminary results demonstrate the ability of small ligands bound to the metal center to alter dramatically the inherent reactivity of gas-phase metal ions. In sharp contrast to the bare metal ions Fe^+, Co^+, and Ni^+, which add nearly exclusively across C–C bonds of linear alkanes, the corresponding metal hydrides favor initial oxidative addition across C–H bonds. Furthermore, it is striking that Co^+ and Ni^+ are rendered more reactive by a hydride ligand bound to the metal center. The apparent order of reactivity $NiD^+ > CoD^+ > FeD^+$ is certainly the opposite of what would be expected on the basis of the bare metal reactivity. The effects of other ligands such as CH_2, CH_3, O, and S on the reactivity of gas-phase metal ions are being actively pursued in our laboratory.

Acknowledgment is made to the Department of Energy (DE-AC02-ER1 0689) for supporting this research and to the National Science Foundation (CHE-8002685) for providing funds to purchase the FTMS. We thank M. B. Wise for constructing a 5.2-cm cubic trapped ion cell.

Synthesis and Structures of $(i\text{-}PrC_5H_4)_2V_2S_4$ and $(C_5H_5)_2V_2S_2(S_2C_2(CF_3)_2)$: The Influence of π-Bonding on the Geometry of the μ-S_2 Ligand

C. Mark Bolinger and Thomas B. Rauchfuss*[1]

School of Chemical Sciences, University of Illinois
Urbana, Illinois 61801

Arnold L. Rheingold*

Department of Chemistry, University of Delaware
Newark, Delaware 19711

Received May 16, 1983

The compound $(MeCp)_2V_2S_4$[2] (MeCp = η^5-methylcyclopentadienyl) has been shown to be useful in the preparation of vanadium sulfide cluster compounds and has proven to be a versatile precursor for a host of other derivatives.[3] Although we have been unable to obtain single crystals of $Cp_2V_2S_4$ or $(MeCp)_2V_2S_4$ suitable for X-ray diffraction, the relatively high symmetry of the V_2S_4 core was suggested by the ^1H NMR spectrum of the MeCp derivative. On the basis of these data and IR measurements, we indicated[3] that precedented structural possibilities for the V_2S_4 core included $V_2(\mu\text{-}\eta^2\text{-}S_2)_2$ (cf. $(VS_4)_n$[4]) and $V_2(\mu\text{-}S)_2(\mu\text{-}\eta^2\text{-}S_2)$ (cf. Wachter's isomer of $(Me_5C_5)_2Mo_2S_4$[5]). In this report we describe the unanticipated (and unprecedented) structures of $(i\text{-}PrCp)_2V_2S_4$ and the acetylene adduct of $Cp_2V_2S_4$. In a broader context, our results provide fresh insights into the important effects of π-bonding in electron-deficient transition-metal compounds.

$(i\text{-}PrCp)_2V_2S_4$ was prepared in three steps from $(i\text{-}PrCp)_2VCl_2$[6] by established procedures[7] and was shown to be closely related to $(MeCp)_2V_2S_4$ based on the superimposability of their optical spectra.[8] The structure[9] of $(i\text{-}PrCp)_2V_2S_4$ (**1**) is depicted in Figure 1. The two $(i\text{-}PrCp)V$ moities are bridged by one $\mu\text{-}\eta^1\text{-}S_2$ and two μ-S ligands. The V···V distance of 2.610 (1) Å is appropriate for a single bond. The average V–S(μ-S) and V–S(S_2) distances

---

[1] Fellow of the Alfred P. Sloan Foundation (1983–1985), Camille and Henry Dreyfus Teacher-Scholar (1983–1988).

[2] Bolinger, C. M.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1982**, *104*, 7313.

[3] (a) Rauchfuss, T. B.; Weatherill, T. D.; Wilson, S. R.; Zebrowski, J. P. *J. Am. Chem. Soc.*, in press. (b) Bolinger, C. M.; Rauchfuss, T. B., unpublished results.

[4] (a) Allmann, R.; Baumann, I.; Kutoglu, A.; Rösch, H.; Hëllner, E. *Naturwissenschaften* **1963**, *51*, 262. (b) Klemm, W.; Schnering, H. G. *Ibid.* **1964**, *52*, 12.

[5] Brunner, H.; Meier, W.; Wachter, J.; Guggolz, E.; Zahn, T.; Ziegler, M. L. *Organometallics* **1982**, *1*, 1107.

[6] Giolando, D. M.; Rauchfuss, T. B., unpublished results.

[7] Bolinger, C. M.; Rauchfuss, T. B.; Rheingold, A. L. *Organometallics* **1982**, *1*, 1551.

[8] Anal.: C, H, V. IR (mineral oil mull) 1418 (m), 1316 (s), 1061 (m), 1046 (s), 925 (s), 818 (vs) cm^{-1}; ^1H NMR (90 MHz, $CDCl_3$) δ 6.87 (m, 2 H), 6.70 (m, 2 H), 3.05 (septet, 1 H, $J_{HH} = 7\ s^{-1}$), 1.38 (d, 6 H, $J_{HH} = 7\ s^{-1}$); electron-impact mass spectrum (70 eV), *m/e* 444 (100%, M^+), 410 (14.6%, $C_{16}H_{20}S_3V_2{}^+$), 376 (85.4%, $C_{16}H_{18}S_2V_2{}^+$); UV–vis (THF) λ_{max} 366 nm (6900 L mol^{-1} cm^{-1}).

[9] $(i\text{-}PrCp)_2V_2S_4$ (**1**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.390$ (3) Å, $b = 10.103$ (2) Å, $c = 18.485$ (5) Å, $\beta = 102.08$ (2)°, $V = 1897.5$ (7) Å^3, $Z = 4$, and $\mu = 13.71\ cm^{-1}$ (Mo K_α). A total of 3255 reflections ($4° \le 2\theta \le 47°$) were collected on a Nicolet R3 diffractometer of which 2799 were unique. Of these reflections 2072 with $F_o \ge 3\sigma(F_o)$ were used in the subsequent direct-methods solution and refinement. The final discrepancy indices with anisotropic refinement of all non-hydrogen atoms were $R_f = 5.90\%$, $R_wF = 5.91\%$, and GOF = 1.420.