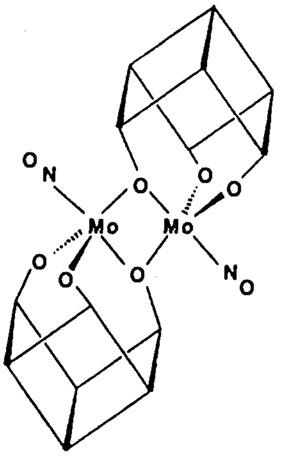
to one *tert*-butoxide ligand are also observed, as well as a resonance at δ 14.33 in the ^1H NMR spectrum, which shows coupling to two inequivalent ^{183}W nuclei (^{183}W, $I = {}^1/_2$, 14.5% natural abundance). We formulate this new ditungsten compound as $[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2W_2(\mu\text{-}H)(O\text{-}t\text{-}Bu)$, an analogue of $[W_2(\mu\text{-}H)(O\text{-}i\text{-}Pr)_7]_2$.[9]

The reaction between III and NO (2 equiv) gives a dinitrosyl complex that possesses (by ^{29}Si and ^{13}C NMR) two equivalent Si_7O_{12} frameworks that are bisected by a molecular plane of symmetry.[10] By analogy to the known reaction chemistry of $Mo_2(OR)_6$ compounds with NO,[11] we formulate this compound as $[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2Mo_2(NO)_2$, of structural type VI, which is formed by cleavage of the M≡M bond. Quite interestingly, ν(NO) for VI occurs at 1670 cm^{-1} in the IR spectrum. This is approximately 30 cm^{-1} higher than ν(NO) observed for analogous alkoxide complexes, indicating that the trisiloxide ligand is a poorer electron donor than three independent alkoxide ligands.[12]



VI

In conclusion, the use of I as a ligand for dinuclear Mo and W complexes has allowed two aspects of the chemistry of the $(M\equiv M)^{6+}$ unit to be seen for the first time. First, the dynamic NMR data for III suggest that the energy required to transform an ethane-like $X_3M\equiv MX_3$ compound to a bridged species may be between 11 and 14 kcal/mol. Second, the facile oxidative addition of an O—H bond to a $(W\equiv W)^{6+}$ center occurs in the absence of a Lewis base.[13] Both of these observations may reflect a bridge-stabilizing ability of the $[(c\text{-}C_6H_{11})_7Si_7O_{12}]^{3-}$ ligand, but further speculation is not warranted at this time. Further studies of the reactivity of these interesting trisiloxy dinuclear compounds are planned.

Acknowledgment. We thank the National Science Foundation for support. T.A.B. thanks the John and Fannie Hertz Foundation for a predoctoral fellowship.

Supplementary Material Available: Listing of atomic coordinates and isotropic thermal parameters, bond angles, and bond distances for $[(c\text{-}C_6H_{11})_6Si_7O_{12}]_2Mo_2$ (M≡M) (14 pages). Ordering information is given on any current masthead page.

---

(8) Selected NMR data for $[(c\text{-}C_6H_{11})_7Si_7O_{12}]_2W_2(\mu\text{-}H)(O\text{-}t\text{-}Bu)$: ^1H NMR (500 MHz, C_6D_6, 25 °C) δ 14.33 [1 H, J_{W-H} = 88 Hz (14%), 120 Hz (16%)]; $^{13}C\{^1H\}$ NMR *(126 MHz, toluene-d_8, 22 °C) δ 26.3, 25.8, 25.6, 24.6, 24.4, 24.3, 24.0, 23.9, 23.8, 23.7, 23.6, 23.5 (1:1:1:1:1:3:1:1:1:1:1:1: for CH), 92.7 ($OCMe_3$), 30.8 ($C\mathit{Me}_3$); $^{29}Si\{^1H\}$ NMR (99 MHz, C_6D_6, 22 °C): δ −60.0, −61.4, −62.0, −62.9, −63.8, −67.3, −67.4, −67.5, −67.6, −68.1, −68.4, −69.2 (1:1:1:1:1:1:1:1:3:1:1:1).

(9) (a) Akiyama, M.; Chisholm, M. H.; Haitko, D. A.; Little, D.; Cotton, F. A.; Extine, M. W. *J. Am. Chem. Soc.* **1979**, *101*, 2504. (b) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Haitko, D. A.; Leonelli, J.; Little, D. *J. Am. Chem. Soc.* **1981**, *103*, 779. (c) Chisholm, M. H.; Huffman, J. C.; Smith, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 222.

(10) Selected NMR data for VI: $^{13}C\{^1H\}$ NMR (126 MHz, toluene-d_8, 22 °C) δ 24.6, 24.3, 24.2, 24.0, 23.7 (1:1:2:2:1 for CH); $^{29}Si\{^1H\}$ NMR (99 MHz, C_6H_6, 22 °C): δ −55.4, −61.4, −63.1, −66.3, −66.8 (2:1:1:2:1).

(11) Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Kelly, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3354.

(12) (a) The electron-withdrawing capabilities of a Si_8O_{12} silasesquioxane framework are comparable to those of a trifluoromethyl (i.e., CF_3) group.[12b] (b) Feher, F. J.; Budzichowsi, T. A. *J. Organomet. Chem.* **1989**, *379*, 33.

(13) This is in contrast to the oxidative addition of *i*-PrOH to $W_2(O\text{-}i\text{-}Pr)_6$ to yield $[W_2(H)(O\text{-}i\text{-}Pr)_7]_2$. See ref 9b.

Requirements for Houben–Hoesch and Gattermann Reactions. Involvement of Diprotonated Cyanides in the Reactions with Benzene

Michihisa Yato, Tomohiko Ohwada, and Koichi Shudo*

Faculty of Pharmaceutical Sciences, University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113, Japan

Received July 18, 1990

Friedel–Crafts acylation with nitriles and HCl (and/or Lewis acids) is called the Houben–Hoesch reaction (eq 1).[1] The

$$ArH + RC\equiv N \xrightarrow{H^+} ArC(=NH)R \xrightarrow{H_2O} ArC(=O)R \qquad (1)$$

Gattermann reaction is a special case in which the nitrile is hydrogen cyanide (R = H).[2] These reactions are generally useful only with phenols, phenolic ethers, and some heterocyclic compounds. The reaction mechanism seems to be complex and is not completely settled.[3] The first stage consists of protonation of a nitrile to a nitrilium ion (**1**) or nitrile–Lewis acid complex. Generally these are regarded as being the electrophilic species attacking the phenols or other activated aromatics.[3] The protonated form (**2**) of the chloro imine is also a candidate electrophile.

$$\underset{\mathbf{1}}{RC\equiv N^+H \leftrightarrow RC^+=NH} \qquad \underset{\mathbf{2}}{RC(Cl)=N^+H_2}$$

The reactions of nitriles with benzene itself have been studied less thoroughly. The original procedure of Gattermann was improved by Hinkel et al:[4] the reaction of hydrogen cyanide with benzene was attained in the presence of an excess amount of HCl and $AlCl_3$ at refluxing temperature. The reaction in the presence of $Zn(CN)_2$–HCl–$AlCl_3$ was examined by Olah et al.[5] In these reactions the monoprotonated species or other stable cationic species such as **1** and **2** cannot be the attacking electrophile toward benzene. In this paper, a simple and generalized procedure and requirements for the Gattermann and Houben–Hoesch reactions are described.

Sodium cyanide and benzene did not react in the presence of 23% trifluoromethanesulfonic acid (TFSA)–77% trifluoroacetic acid (TFA) ($H_0 = -10.6$, 450 equiv with respect to the cyanide).[6] Heightening of the acidity was required for the reaction to occur. In TFSA ($H_0 = -13.7$), the reaction proceeded within 30 min and the yield reached 44% (determined after aqueous acid hydrolysis to benzaldehyde). Addition of 1% SbF_5 to TFSA ($H_0 = -16.8$) speeded up the reaction. In the presence of 5% SbF_5, the reaction was instantaneous and the yield was excellent (Table I).

In order to eliminate the complexity arising from the use of sodium cyanide, trimethylsilyl cyanide was chosen as the cyanide.

---

(1) Hoesch, K. *Ber. Dtsch. Chem. Ges.* **1915**, *48*, 1122. Houben, J. *Ber. Dtsch. Chem. Ges.* **1926**, *59*, 2878. Ruske, W. *Friedel–Crafts and Related Reactions*; Olah, G. A., Ed.; Wiley-Interscience: New York, 1964; Vol. III, Part I, Chapter 32.

(2) Gattermann, L. *Ber. Dtsch. Chem. Ges.* **1898**, *31*, 1149.

(3) Jeffery, E. A.; Satchell, D. P. N. *J. Chem. Soc. B* **1966**, 579. Booth, B. L.; Noori, G. F. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2894. Amer, M. I.; Booth, B. L.; Noori, G. F.; Proença, M. F. J. R. P. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1075.

(4) Hinkel, L. E.; Ayling, E. E.; Morgan, W. H. *J. Chem. Soc.* **1932**, 2793.

(5) Olah, G. A.; Ohhannesian, L.; Arvanaghi, M. *Chem. Rev.* **1987**, *87*, 571. Olah, G. A.; Pelizza, F.; Kobayashi, S.; Olah, J. A. *J. Am. Chem. Soc.* **1976**, 98.

(6) The acidity function H_0 of TFA–TFSA was determined by a modification of the procedure previously described using a set of nitroanilines and nitrobenzenes as Hammett's indicators with UV detection. Experimental details will be reported elsewhere.

0002-7863/91/1513-691$02.50/0

Table I. Acid-Catalyzed Reactions of Nitriles with Benzene[a]

run	nitrile	acid[c]	$-H_0$[d]	time, min	phenylated product
1	HCN[b]	23% TFSA–77% TFA	10.6	300	0
2	HCN[b]	55% TFSA–45% TFA	11.8	300	3
3	HCN[b]	80% TFSA–20% TFA	12.7	300	11
4	HCN[b]	TFSA	13.7	30	44
5	HCN[b]	99% TFSA–1% SbF_5	16.8	30	65
6	HCN[b]	95% TFSA–5% SbF_5	>18	5	92
7	$(CH_3)_3SiCN$	55% TFSA–45% TFA	11.8	300	2
8	$(CH_3)_3SiCN$	80% TFSA–20% TFA	12.7	30	17
9	$(CH_3)_3SiCN$	TFSA	13.7	30	55
10	$(CH_3)_3SiCN$	95% TFSA–5% SbF_5	>18	5	99
11	PhCN	55% TFSA–45% TFA	11.8	300	11[e]
12	PhCN	TFSA	13.7	120	14[f]
13	PhCN	95% TFSA–5% SbF_5	>18	30	54[g]

[a] All the reactions were performed at 20 °C. [b] Sodium cyanide was used as a source of HCN. [c] Compositions of mixed acids are given in weight percentages. In all the reactions, a 450-fold molar excess of the acid was used. [d] Footnote 6. [e] Accompanied by a 15% yield of PhCN and 17% of 2,4,6-triphenyltriazine. [f] Accompanied by a 50% yield of PhCN. [g] Accompanied by a 29% yield of PhCN.

The reaction with benzene in the presence of the acid proceeded in a very similar way to the case of hydrogen cyanide. Here again, a strong acid is required, and the higher the acidity is, the better the result. Though attempts to find good conditions for the reaction of acetonitrile with benzene were unsuccessful, we could react benzonitrile with benzene. In the presence of a weak acid system, the yield of benzophenone obtained after hydrolysis of the product was very low, but in a medium of higher acidity, significant formation of benzophenone was attained (Table I).

In all cases, very high acidity is required for the reaction. The Lewis acid functions so as to raise the acidity, but seems to have no special role, because the reaction definitely proceeds in neat TFSA. Since the basicity (pK_{BH^+}) of nitriles is around −10 to −11 (−10.5 for benzonitrile and −10.12 for acetonitrile),[7] the nitriles in 23% TFSA–77% TFA are roughly half-protonated. In an acid system with $H_0 < -12$, monoprotonation should be almost complete. Nevertheless, further increase of the acidity is very favorable for the reactions, implying that additional protonation on the monoprotonated species **1** is required for the reactions.

In order to obtain further evidence for the participation of the second protonation, the reaction of *N*-methylbenzonitrilium triflate (**3**)[8] with benzene was analyzed. This ion reacts with activated

$$PhC{\equiv}N^+CH_3$$

3

aromatics,[8] but does not react with benzene even in the presence of TFA. TFSA can catalyze the reaction, but only very slowly (20 h) and in low yield (3%). The stronger acid TFSA–SbF_5 (5%) was acidic enough to allow the reaction to proceed, and benzophenone (55%) was isolated. This definitely indicates that protonation is required for the reaction with benzene.

Thus, it is concluded that the reactive species, the dication **4**, is formed by protonation of N-protonated or N-alkylated nitriles in the highly acidic media. The stable nitrilium ion or a carbocation stabilized by an imino group is protonated to form a carbocation (**4**) *destabilized* by an iminium cation group. This activation of the carbocation makes the reaction proceed.

$$RC^+{=}N^+H_2$$

4

The electronic nature of the species has been fully analyzed by Schwarz et al.[9] According to the calculations for the diprotonated hydrogen cyanide H_3CN^{2+}, the N,N-diprotonated planar structure is preferable to the C,N-diprotonated one. The N,N-diprotonated species bears more positive charge on the carbon atom than does the latter. The dicationic species is more energetic than the monocation and thus can react readily with benzene.

The present understanding of the Houben–Hoesch and Gattermann reactions can be extended to some Friedel–Crafts type reactions.[10] Since C-protonated carbon monoxide is isosteric with hydrogen cyanide, the Gattermann–Koch reaction is suspected to involve the diprotonated carbon monoxide[11] as the electrophile.

---

(7) Deno, N. C.; Gaugler, R. W.; Wisotsky, M. J. *J. Org. Chem.* **1966**, *31*, 1967. Olah, G. A.; Kiorsky, T. E. *J. Am. Chem. Soc.* **1968**, *90*, 4666.

(8) Booth, B. L.; Jibodu, K. O.; Proença, M. F. *J. Chem. Soc., Chem. Commun.* **1980**, 1151.

(9) Koch, W.; Heinrich, N.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 5400.

(10) Olah, G. A.; Prakash, S.; Lammertsma, K. *Res. Chem. Intermed.* **1989**, *12*, 141.

(11) Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1983**, *105*, 5484.

Raman Spectrum of Matrix-Isolated Cyclobutadiene. Evidence for Environmental Hindrance to Heavy-Atom Tunneling?

Bradley R. Arnold, Juliusz G. Radziszewski, Alan Campion,
Scott S. Perry, and Josef Michl*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712-1167

Received April 17, 1990

We have recorded the Raman spectrum of matrix-isolated cyclobutadiene (**1**)[1] as a function of temperature and find that it agrees much better with expectations for a rectangular species with a harmonic force field than those for a species tunneling at the previously computed[2] very rapid rates ($\sim 10^{11}$ s^{-1}) between two rectangular geometries.

Matrix-isolated cyclobutene-3,4-dicarboxylic anhydride (**2**) produces **1**, CO, and CO_2 upon 254-nm irradiation.[3] We have also detected the byproducts **3**–**5** by their IR spectra in Ar and Ne matrices. Simultaneous irradiation at 254 and 313 nm (Mineralight lamp UVGL25, with filter removed) destroys the byproducts and removes all UV absorption peaks above 230 nm while converting a minor fraction of **1** to acetylene. The use of a sapphire substrate permits simultaneous observation of the UV spectrum and the C–H stretching bands in the IR spectrum of

---

(1) For recent reviews, see: (a) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 309. (b) Arnold, B.; Michl, J. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, NY, 1990; Chapter 1, p 1.

(2) (a) Carpenter, B. K. *J. Am. Chem. Soc.* **1983**, *105*, 1700. (b) Huang, M.-J.; Wolfsberg, M. *J. Am. Chem. Soc.* **1984**, *106*, 4039. (c) Dewar, M. J. S.; Merz, K. M., Jr.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1984**, *106*, 4040. (d) Čársky, P.; Bartlett, R. J.; Fitzgerald, G.; Noga, J.; Špirko, V. *J. Chem. Phys.* **1988**, *89*, 3008. (e) Čársky, P.; Špirko, V.; Hess, B. A., Jr.; Schaad, L. J. *J. Chem. Phys.* **1990**, *92*, 6069. (f) Čársky, P.; Downing, J. W.; Michl, J. *Int. J. Quantum Chem.* In press.

(3) Maier, G.; Hartan, H.-G.; Sayrac, T. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 226.