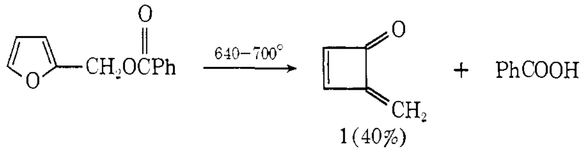
Formation of Methylenecyclobutenone from the Pyrolysis of Furfuryl Benzoate

Sir:

We wish to report that the low pressure (*ca.* 10^{-4} Torr) gas-phase pyrolysis[1] of furfuryl benzoate[2] gives a substantial yield of methylenecyclobutenone (**1**), the parent of a relatively uncommon system.[4]

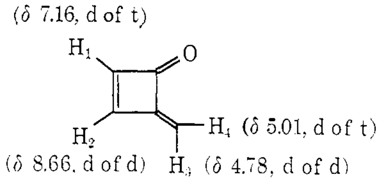


1(40%)

Methylenecyclobutenone is easily separated from the benzoic acid since the benzoic acid crystallizes at the top of the trap, which is cooled with liquid nitrogen, and **1** condenses at the bottom of the trap. If the trap is warmed before solvent is added, the liquid phase, which is largely **1**, polymerizes to a plastic-like material. This is the same behavior that was noted for neat isopropylidenecyclobutenone (**2**).[4] However, if chloroform or ethyl acetate is added to the trap before warming, a solution of **1** is obtained which is stable enough to handle at room temperature and is stable for weeks when kept at *ca.* −10°. Nmr analyses of these solutions show reasonably pure **1** with very small amounts of benzene, starting ester, and other minor products.

The structure of **1** is based on its ir and nmr spectra and its conversion to 2-methylcyclobutanone by catalytic hydrogenation. The ir spectrum ($CDCl_3$) of **1** shows a strong carbonyl absorption at 1783 cm^{-1} which agrees very well with that reported for cyclobutenone (**3**), 1790 cm^{-1},[5] and cyclobutanone, 1780 cm^{-1},[6] but is somewhat higher than that reported for **2**, 1740 cm^{-1} (neat),[4] and 2-methylenecyclobutanone (**4**), 1765 cm^{-1}.[7] The ir spectrum of **1** also contains strong bands at 1688 (C=C) and 823 ($C{=}CH_2$) cm^{-1}.

The nmr spectrum (EtOAc) of **1** consists of four multiplets of equal intensity. Coupling constants were determined by expansion of each multiplet ($J_{12} = 2.75$, $J_{13} = J_{14} = 0.7$, $J_{23} = 0.0$, $J_{24} = 0.7$, $J_{34} = 1.35$ Hz) and the nmr data are summarized as follows



The chemical shifts of H_1 and H_2 are similar to those of the corresponding protons of **2**, δ 6.82 and 8.78, respectively,[4] and **3**, δ 6.7 and 8.35, respectively.[5] Moreover, the coupling constant between these two protons for **1** is very close to those reported for **2**, 3.0 Hz,[4] and **3**, 2.5 Hz.[5] The chemical shifts of H_3 and H_4 are very similar to those reported for **4**, δ 5.11 and 5.67.[7] The lower field signal was assigned to H_4 since it should be more deshielded by the carbonyl group as it is closer to it.

A quantity of 2.0 mmol of **1** in ethanol–ethyl acetate was hydrogenated using palladium/carbon as the catalyst. After 4.3 mmol of hydrogen was taken up, the reduction slowed down considerably. The ir and nmr spectra of the hydrogenation product, which was purified by glpc, matched exactly those reported for 2-methylcyclobutanone.[8]

Pyrolyses of 160-mg samples of furfuryl benzoate were carried out with the column temperature at 640–700°, head temperature at 30–40°, and pressure at *ca.* 10^{-4} Torr. The pyrolyses took 2–3 hr. After the pyrolysis, a known amount of an internal standard, 1,2-dibromoethane, and chloroform-*d* were added to the trap and the yield of **1** was determined by nmr analysis. For three runs, 38–40% **1**, 3% benzene, 1% starting ester, and traces of other materials were obtained.

The mechanism of the formation of **1** and extension of this reaction to substituted furfuryl esters are under active investigation.

Walter S. Trahanovsky,* Myong-Gi Park
Department of Chemistry
Iowa State University of Science and Technology
Ames, Iowa 50010

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(1) Pyrolyses were carried out as described by W. S. Trahanovsky, C. C. Ong, J. G. Pataky, F. L. Weitl, P. W. Mullen, J. C. Clardy, and R. S. Hansen, *J. Org. Chem.*, **36**, 3575 (1971).

(2) This ester was synthesized from furfuryl alcohol and benzoyl chloride: nmr (neat) δ 8.82–7.83 (m, 2, *o*-phenyl), 7.38 (m, 1, H_5), 7.33–7.00 (m, 3), 6.44 (br d, $J = 3.2$ Hz, H_3), 6.26 (d of d, $J = 3.2$ Hz, $J' = 1.8$ Hz, H_4), and 5.30 (s, 2); ir (CCl_4) 1720 (vs), 1265 (vs), 1250 (vs), 1105 (s), and 1090 (s) cm^{-1}; bp 117–119° (1.5 mm) (lit.[3] bp 275–285° (760 mm)).

(3) L. von Wissel and B. Tollens, *Justus Liebigs Ann. Chem.*, **272**, 301 (1892).

(4) R. C. De Selms and F. Delay, *J. Amer. Chem. Soc.*, **95**, 274 (1973), and references cited therein.

(5) J. B. Sieja, *ibid.*, **93**, 2481 (1971).

(6) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, Calif., 1962, p 42.

(7) M. Mühlstädt and H. Meinhold, *J. Prakt. Chem.*, **37**, 162 (1968).

(8) H. H. Wasserman, R. E. Cochoy, and M. S. Baird, *J. Amer. Chem. Soc.*, **91**, 2375 (1969).

Lewis Acidic Metal Alkyl–Transition Metal Complex Interactions. I. Niobium and Tantalum Hydrides

Sir:

Lewis acidic metal alkyls, especially those of aluminum, are widely used on an empirical basis as "promoters" of reactions catalyzed by transition metal complexes, but generally little is known about the interactions involved.[1] In this article we characterize in detail the reactions of dicyclopentadienylniobium and -tantalum hydrides with alkyls of aluminum, gallium, zinc, cadmium, and hafnium.[2,3] The products are either simple Lewis acid–base adducts or compounds formed by alkane elimination from these adducts. Compounds isolated in a pure crystalline form are presented in Table I.

Triethylaluminum reacts rapidly with cyclopentadienylniobium and -tantalum hydrides in benzene solu-

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(1) (a) The Lewis basicity of transition metal complexes is reviewed by J. C. Kotz and D. G. Pedrotty, *Organometal. Chem. Rev. A*, **4**, 479 (1969), and by D. F. Shriver, *Accounts Chem. Res.*, **3**, 231 (1970); (b) reactions of metal carbonyls with Lewis acids are reviewed by D. F. Shriver and A. Alich, *Coord. Chem. Rev.*, **8**, 15 (1972).

(2) Other well-characterized hydride reactions are those of Cp_2WH_2,[3a] Cp_2ReH,[3a] Cp_2ZrH_2,[3b] and $CpMoH(CO)_2PR_3$[3c] with group IIIa alkyls.

(3) (a) H. Brunner, P. C. Wailes, and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **1**, 125 (1965); (b) P. C. Wailes, H. Weigold, and A. P. Bell, *J. Organometal. Chem.*, **43**, C29 (1972); (c) W. R. Kroll and G. B. McVicker, *Chem. Commun.*, 591 (1971).

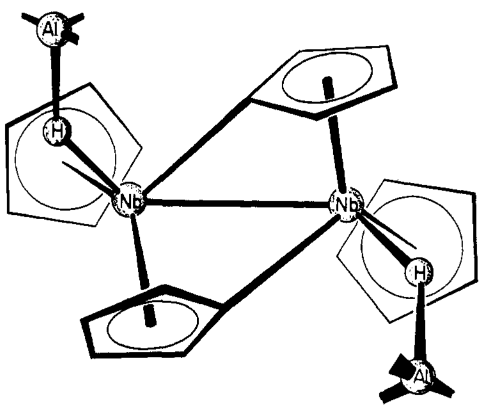

Figure 1. The proposed structure of $[(C_5H_5)(C_5H_4)NbHAl(C_2H_5)_3]_2$ (**1**). The structure is presumed to be closely related to that of $[(C_5H_5)(C_5H_4)NbH]_2$[6] and $[(C_5H_5)(C_5H_4)TiHAlEt_2]_2$ (F. N. Tebbe and L. J. Guggenberger, *J. Chem. Soc., Chem. Commun.*, 227 (1973)).

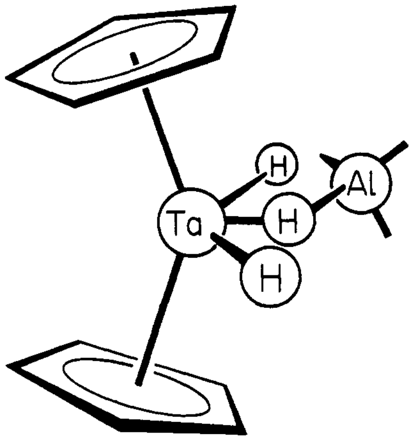

Figure 2. The proposed structure of $(C_5H_5)_2TaH_3Al(C_2H_5)_3$ (**5**).

Table I. Properties of Aluminum and Zinc Derivatives of Niobium and Tantalum Hydrides

No.	Compound[a]	Calcd for C, H (found)	Mol wt calcd (found)[b]	Hydride nmr, τ[c]
1	$(CpC_5H_4NbH\text{-}AlEt_3)_2\cdot 0.96C_8H_{10}$[d]	61.3, 7.7 (61.1, 7.9)	396[d] (404)	17.02
2	$Cp_2Nb\begin{array}{l}\diagup HAlEt_3\\ \diagdown (CH_2{=}CH_2)\end{array}$	59.0, 8.3 (58.9, 8.3)	366 (369)	19.63
3	$Cp_2Nb\begin{array}{l}\diagup HAlEt_3\\ \diagdown CO\end{array}$	55.7, 7.2 (55.6, 7.2)	366 (359)	21.51
4	$Cp_2Nb\begin{array}{l}\diagup HAlEt_3\\ \diagdown PMe_3\end{array}$	55.1, 8.5 (54.8, 8.5)	414 (399)	23.12
5	$Cp_2TaH_3AlEt_3$	44.9, 6.6 (44.4, 6.3)	428 (419)	14.68 (A) 12.46 (B_2) J_{AB} = 12.3 Hz
6	$Cp_2NbH_2AlEt_2$	54.2, 7.2 (54.3, 7.3)	310 (310)	22.78
7	$(Cp_2NbH_2)_2Zn$	46.6, 4.7 (46.5, 4.7)	516 (507)	19.05

[a] Cp = C_5H_5. All of the compounds are extremely reactive with air, and are to be regarded as pyrophoric. [b] Cryoscopic, in benzene, for **1**–**5** and **7**; mass spectrometric for **6**. [c] C_6D_6 solvent, 220 MHz. [d] C_8H_{10} = *o*-xylene of solvation, determined by ^1H nmr. The calcd mol wt is based on dissociation of the solvate in benzene solution.

tion at room temperature to form strong adducts[4] according to (1)–(3) (Cp = C_5H_5).

$$[CpC_5H_4NbH]_2{}^{5,6} \xrightarrow{2Et_3Al} \underset{\textbf{1}}{[CpC_5H_4NbHAlEt_3]_2} \qquad (1)$$

$$Cp_2NbLH^6 \xrightarrow{Et_3Al} Cp_2NbLHAlEt_3 \qquad (2)$$

$$L = C_2H_4,\ \textbf{2};\ CO,\ \textbf{3};\ Me_3P,\ \textbf{4}$$

$$Cp_2TaH_3{}^7 \xrightarrow{Et_3Al} \underset{\textbf{5}}{Cp_2TaH_3AlEt_3} \qquad (3)$$

It is probable that Et_3Al bonds to the niobium complex at the hydride sites in **1** (Figure 1) and **2**, forming hydride-bridged systems, Nb–H–Al.[8] Coordination of Et_3Al with the hydridic ligands in $[CpC_5H_4NbH]_2$ and $Cp_2Nb(C_2H_4)H$ produces hydride nmr shifts to high field of 5 and 7 ppm, respectively; other resonances in the spectra are affected only slightly. Similar hydride shifts occur upon coordination of $Cp_2Nb(CO)H$ and $Cp_2Nb(PMe_3)H$, suggesting Nb–H–Al interactions in **3** and **4**. However, **3** and **4** could also exist as Nb–Al bonded structures related to $Cp_2WH_2AlMe_3$, for which W–Al bonding was proposed.[3a,9]

The adduct **5** presents a different structural problem in that two types of hydride sites are potentially available for coordination. Only the A portion of the AB_2 hydride nmr spectrum of Cp_2TaH_3 is affected by coordination with Et_3Al, suggesting selective interaction at the unique hydrogen (Figure 2).[10]

The $Cp_2TaH_3GaEt_3$ adduct appears analogous to **5**. Weaker adducts of Cp_2TaH_3 are formed with Et_2Zn and Et_2Cd. Hydride nmr spectra of the zinc system, unlike those for **5**, are temperature dependent between 40 and −50°. Diethylzinc is removed from the system by repeated crystallization. These data define the equilibrium process.

$$Cp_2TaH_3 \underset{-Et_2Zn}{\overset{Et_2Zn}{\rightleftharpoons}} Cp_2TaH_3ZnEt_2 \qquad (4)$$

Adducts of Cp_2NbH_3 analogous to those of Cp_2TaH_3 are detected by nmr at −20 to −50°. At room temperature, however, alkane is briskly evolved from the niobium adducts to produce a different type of compound.[11] The reactive tetrabenzylhafnium produces toluene at room temperature upon mixing with solutions of either Cp_2TaH_3 or Cp_2NbH_3.

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(4) The adducts are undissociated in freezing benzene (Table I). In solutions maintained in the dark they are stable (10% or less decomposition) for at least 1 week at room temperature.

(5) F. N. Tebbe and G. W. Parshall, *J. Amer. Chem. Soc.*, **93**, 3793 (1971).

(6) L. J. Guggenberger, *Inorg. Chem.*, **12**, 294 (1973).

(7) M. L. H. Green, J. A. McCleverty, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 4854 (1961).

(8) Direct Nb–Al interaction is unlikely since the metal atoms in $(CpC_5H_4NbH)_2$ and $Cp_2Nb(C_2H_4)H$ are viewed as coordinatively saturated.

(9) Adduct formation with $Cp_2Nb(CO)H$ produces no significant shift in $\nu(C{\equiv}O)$. This excludes significant Al–O interaction in **3**. See ref 1b.

(10) Nmr data do not absolutely rule out Et_3Al interactions at other hydride sites.

(11) Compounds **6** and **7** are stable at room temperature for at least 1 week. The $Cp_2MH_2Hf(CH_2Ph)_3$ derivatives decompose with half lives of the order of hours.

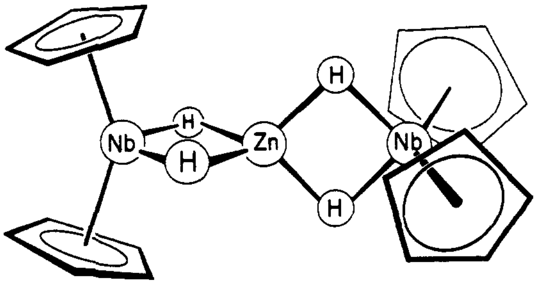

Figure 3. The proposed structure of $[(C_5H_5)_2NbH_2]_2Zn$ (**7**).

$$Cp_2NbH_3 \xrightarrow[-C_2H_6]{Et_3Al} Cp_2NbH_2AlEt_2 \quad (5)$$

6

$$2Cp_2NbH_3 \xrightarrow[-2C_2H_6]{Et_2Zn} (Cp_2NbH_2)_2Zn \quad (6)$$

7

$$Cp_2MH_3 \xrightarrow[-PhCH_3]{(PhCH_2)_4Hf} Cp_2MH_2Hf(CH_2Ph)_3 \quad (7)$$

$$M = Nb \text{ or } Ta$$

Nmr data (25 to −50°) for these compounds require location of the group IIb, IIIa, or IVb metal on the twofold axis of the Cp_2MH_2 moiety. The proposed structure for **7** is presented in Figure 3.

Catalysis of olefin reactions by group IVb complexes is often promoted by Lewis acids. It is of interest to determine the effect of Et_3Al on the ethylene reaction with a group V complex[5]

$$Cp_2Nb(C_2H_4)H \xrightarrow{C_2H_4} Cp_2Nb(C_2H_4)C_2H_5 \quad (8)$$

Under conditions (45°, $P\ C_2H_4 \simeq 5$ atm) where reaction 8 proceeds to 35% completion, ethylene is unreactive with $Cp_2Nb(C_2H_4)HAlEt_3$. Triethylaluminum *deactivates* the hydride ligand toward the ethylene insertion reaction. Investigation of the effects of Lewis acids on other transition metal hydride reactions is in progress.

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Fred N. Tebbe
Contribution No. 2018, Central Research Department
Experimental Station, E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

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Bis Deprotonation of Bridged Bicyclic Sulfones. Electronic Interactions in Rigid Bridgehead α-Sulfonyl Dicarbanions as a Function of Carbon Framework Unsaturation[1]

Sir:

Conformationally constrained cyclic α-sulfonyl carbanions do not share with their acyclic counterparts the intrinsic ability to maintain configurational stability owing to an enhanced propensity for symmetrization *via* effectively planar conformations.[2] Bridgehead α-sulfonyl carbanions[3] have no such capability and furthermore may be viewed as essentially pyramidal intermediates with the carbon lone pair orbital directed along the bisector of the OSO angle. LCAO-MO-SCF calculations have shown this particular alignment to be the most stable of a number of conformations examined.[4] In this connection, the recent availability of variously unsaturated derivatives of 9-thiabicyclo[4.2.1]nonane 9,9-dioxide (**1**) such as **2**–**5**[5–7] has attracted our attention not only as valuable synthetic intermediates[5a,b,8] but also as possible sources of interesting stereochemically rigid α-sulfonyl dicarbanions. Herein we detail the unique electronic interactions which operate upon bis deprotonation of these bridged bicyclic sulfones.

Preliminary information on the capability of **1**–**5** for dianion formation and the inherent stability of these species was gained by adding *n*-butyllithium in pentane (25% excess) to 0.1 *M* solutions of these sulfones in anhydrous tetrahydrofuran cooled to −70° under a dry nitrogen atmosphere. A large excess of DOAc (>95% isotopic purity) was subsequently introduced and the sulfone recovered by silica gel chromatography.[9] The results, summarized in Table I, reveal three points of major significance: (a) generation of **1**$^{2-}$ is comparatively sluggish (moderate level of exchange after 60 min), (b) **4**$^{2-}$ is relatively unstable; and (c) **5**$^{2-}$ is exceptionally highly colored, the intense purple hue being independent of the method of dianion generation.[10]

Comparable experiments, but with substitution of methyl iodide for the DOAc, led exclusively to 1,6-dimethyl sulfones.[11] Yields of the dimethyl products ran as follows: **1** (91%), **2** (88%), **3** (80%), **4** (50%), **5** (95%). No evidence was gained for the formation of monomethylated sulfones.

From the available data, it is apparent that in the dianions generated from **2**–**5** there are transitions of sufficiently low energy as to be observed in the visible region of the electronic spectrum. To rationalize this we have carried out semiempirical calculations of the extended Hückel (EH) type.[12–14] Based on

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[1] Unsaturated Heterocyclic Systems. XCII. The preceding paper in this series is L. A. Paquette, M. J. Broadhurst, C. Lee, and J. Clardy, *J. Amer. Chem. Soc.*, **95**, 4647 (1973).

[2] (a) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Lett.*, 515 (1962); (b) D. J. Cram and T. A. Whitney, *J. Amer. Chem. Soc.*, **89**, 4651 (1967); (c) L. A. Paquette, J. P. Freeman, and M. J. Wyvratt, *ibid.*, **93**, 3216 (1971).

[3] (a) W. von E. Doering and L. K. Levy, *ibid.*, **77**, 509 (1955); (b) L. A. Paquette and R. W. Houser, *ibid.*, **91**, 3870 (1969); (c) E. J. Corey and E. Block, *J. Org. Chem.*, **34**, 1233 (1969).

[4] S. Wolfe, A. Rauk, and I. G. Csizmadia, *J. Amer. Chem. Soc.*, **91**, 1568 (1969).

[5] (a) L. A. Paquette, R. E. Wingard, Jr., and R. H. Meisinger, *ibid.*, **93**, 1048 (1971); (b) L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *ibid.*, **95**, 2230 (1973); (c) J. Gasteiger and R. Huisgen, **94**, 6541 (1972).

[6] W. L. Mock, *ibid.*, **92**, 3807 (1970).

[7] E. D. Weil, K. J. Smith, and R. J. Gruber, *J. Org. Chem.*, **31**, 1669 (1966).

[8] L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Amer. Chem. Soc.*, **94**, 9224 (1972).

[9] Suitable control experiments established that the integrity of the isotopic purity was maintained during the chromatographic purification. Furthermore, the sulfones could be recovered quantitatively by this technique.

[10] Other base-solvent systems examined include potassium *tert*-butoxide in dimethyl sulfoxide or tetrahydrofuran (25°).

[11] All new compounds gave acceptable (±0.3%) combustion data and compatible spectra.

[12] The Slater exponents and ionization potentials were those reported in the literature[13] except in the case of H for which a Slater ex-