92 to 44 Hz." An eight-line ^{13}C nmr spectrum was previously reported, which "completely verifies the rigidity of the ring since it establishes beyond cavil the doubling of methyl and benzylic methylene carbon resonances."[1] Both spectra are distinctly different from those obtained for hydrocarbon **4**, which are displayed in Figures 1 and 2.[9,10] The mass spectrum of the hydrocarbon **4** (prepared by Scheme I) (M^+ *m/e* 292.219200, major ions at *m/e* 201, 200, 109, 105, 97, and base peak 91) is consistent with the assigned structure (calcd M^+ *m/e* 292.219090).

The ^1H nmr spectrum of **4** is temperature dependent (Figure 1). Use of the Gutowsky-Holm equation[11] to obtain rate constants for the site exchange of the methyl group protons and of the benzylic methylene group protons (Figure 1) leads to values for $\Delta G^{\ddagger}$ of *ca.* 11.8 and 11.9 kcal/mol, respectively. These values fall within the normal range of values determined for ring inversion in similarly substituted cyclohexanes.[12]

While the present results do not clarify the nature of the substance obtained by the earlier authors[1,2] and presumed by them to be **4**,[12a] they do establish beyond cavil that **4** does not maintain an "immobile chair conformation" as claimed.[1] By the same token, the rationale advanced[1] to account for the "exceedingly rigid chair" of **4** must be abandoned.

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[9] ^1H nmr: $\delta_{CS_2}^{TMS}$ 0.71 (s, CH_3), 1.31 (m, CH_2), 2.53 (s, $CH_2C_6H_5$), and 6.87–7.25 (m, C_6H_5). Essentially the same spectrum was observed using $CDCl_3$ or $CFCl_3$ as solvent.

[10] ^{13}C nmr (excluding the unsaturated carbon region): δ ^{13}C from dioxane 38.74, 38.14, 37.27, 32.00, 29.49, and 22.66 ppm at *ca.* 40°. These values may be corrected to chemical shifts from benzene by the following equation: δ (from C_6H_6) = δ (from dioxane) + 61.44 ppm.

[11] This method of calculation of $\Delta G^{\ddagger}$ is judged to be sufficiently accurate for the present case. See, for example, D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).

[12] I. O. Sutherland, *Annu. Rep. NMR Spectrosc.*, 4, 71 (1971).

[12a] NOTE ADDED IN PROOF. After the present work was completed, we were informed that this question has since been answered by R. H. Levin, J. D. Roberts, H. Kwart, and F. Walls, *J. Amer. Chem. Soc.*, **94**, 6856 (1972). We thank Professor Roberts for agreeing to publish these results concurrently with ours.

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Dinitrogen Complexes of Molybdenum(I)

Sir:

We wish to report the first examples of a molybdenum(I) cation containing coordinated dinitrogen. The only other reported molybdenum(I)–dinitrogen complex is $MoCl(N_2)(diphos)_2$[1] (where diphos = 1,2-bis-diphenylphosphinoethane).

The addition of solid $Mo(N_2)_2(diphos)_2$[2] (1.0 mmol) to a methanol solution of iodine (3.5 mmol) under dinitrogen produced a red precipitate I, formulated as $[Mo(N_2)_2(diphos)_2]^+I_3^-$, in 90% yield. *Anal.* Calcd for I: C, 47.0; H, 3.6; N, 4.2; I, 28.9. Found: C, 47.3; H, 3.7; N, 3.4; I, 28.9. The complex I is stable in dry air but decomposes readily in solution. In fact the preparation of I could only be carried out under heterogeneous conditions. Attempts to oxidize $Mo(N_2)_2(diphos)_2$ in benzene with iodine gave products containing no dinitrogen.

The infrared spectrum of I showed a strong absorption at 2043 cm^{-1} due to the $\nu(N\equiv N)$ stretching vibration. The increase of $\nu(N\equiv N)$ from 1976 cm^{-1} for $Mo(N_2)_2(diphos)_2$ to 2043 cm^{-1} for I supports an increase in the formal oxidation state of molybdenum ($Mo^0 \rightarrow Mo^+$).

Magnetic susceptibility measurements of I gave a spin-only value for μ_{eff} (uncorrected for diamagnetism) at 25° of 1.97 BM. This value is comparable to the 1.66 BM value reported for the isoelectronic $[Mo(CO)_2(diphos)_2]I_3$[3] and indicates a spin of $^1/_2$.

I could be reduced to the original $Mo(N_2)_2(diphos)_2$ with sodium amalgam in benzene or tetrahydrofuran (40 and 45% yields, respectively), under dinitrogen. However, under argon, no dinitrogen-containing product was isolated.

The reversibility of the oxidation of $Mo(N_2)_2(diphos)_2$ was established by cyclic voltammetry. The voltammogram was run with 10^{-3} *F* dimethylformamide solutions containing 10^{-1} *F* tetraethylammonium perchlorate as supporting electrolyte at a platinum electrode. Scans were run in the range +0.43 to −0.65 V *vs.* a standard calomel electrode with a scan time of 10.00 Hz. $Mo(N_2)_2(diphos)_2$ gave an anodic peak potential at −0.20 V on the forward scan and a cathodic peak potential at −0.27 V on the reverse scan. Similarly, $Mo(N_2)_2(arphos)_2$[4] (where arphos = 1-diphenylarsino-2-diphenylphosphinoethane) gave a scan with peaks at −0.19 and −0.26 V, respectively. Controlled potential coulometry and conductivity measurements were unsuccessful due to the extensive decomposition of I in solution, over a period of time.

The infrared, analytical, and magnetic susceptibility data support the formulation of I as *trans*-$[Mo(N_2)_2(diphos)_2]^+I_3^-$. However, an alternative formulation that does not conflict with the observed data is $\{\mu\text{-}N_2\text{-}[Mo(N_2)(diphos)_2]_2\}^{2+}(I_3^-)_2$ (II). *Anal.* Calcd for II: C, 47.4; H, 3.7; N, 3.2; I, 28.9. The bridging dinitrogen and the two terminal dinitrogen ligands in II would have to be linear (mutually trans) to be consistent with the one $\nu(N\equiv N)$ stretching vibration observed in the infrared spectrum. Efforts to locate the $\nu(N\equiv N)$ stretching vibrations in the Raman have been unsuccessful as a result of the rapid loss of dinitrogen due to interaction with the laser light (4880 Å). The $Mo(N_2)_2(diphos)_2$ complex was also oxidized in benzene by hydrogen chloride and by hydrogen bromide to give either $[Mo(N_2)_2(diphos)_2]^+Cl^-$ and $[Mo(N_2)_2(diphos)_2]^+Br^-$ or the analogous dinitrogen dimer of II. The reaction with chlorine yielded no dinitrogen-containing species. Metal ions such as silver(I) and copper(II), which have been used for the

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[1] L. K. Atkinson, A. H. Mawby, and D. C. Smith, *Chem. Commun.*, 157 (1971).

[2] (a) J. Chatt and A. G. Wedd, *J. Organometal. Chem.*, **27**, C15 (1971); (b) M. Hidai, K. Tominari, and Y. Uchida, *J. Amer. Chem. Soc.*, **94**, 110 (1972).

[3] J. Lewis and R. Whyman, *J. Chem. Soc.*, 5486 (1965).

[4] T. A. George and C. D. Seibold, *Inorg. Nucl. Chem. Lett.*, **8**, 465 (1972).

oxidation of osmium and rhenium dinitrogen complexes,[5] led to the loss of dinitrogen in this case.

The $Mo(N_2)_2(arphos)_2$ complex was also oxidized by iodine,[4] hydrogen chloride, and hydrogen bromide. The infrared data are presented in Table I.

Table I. $\nu(N{\equiv}N)$ Stretching Vibration (cm^{-1}) for the Dinitrogen Complexes of Molybdenum(I) (Nujol Mull)

Starting complex	Oxidizing agent	$\nu(N{\equiv}N)$ of the product
$Mo(N_2)_2(diphos)_2$	I_2	2043 s
$Mo(N_2)_2(diphos)_2$	HCl	2047 s
$Mo(N_2)_2(diphos)_2$	HBr	2047 s
$Mo(N_2)_2(arphos)_2$	I_2	2043 s
$Mo(N_2)_2(arphos)_2$	HCl	2052 s
$Mo(N_2)_2(arphos)_2$	HBr	2052 s

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(5) J. Chatt, J. R. Dilworth, H. P. Gunz, G. J. Leigh, and J. R. Sanders, *Chem. Commun.*, 90 (1970).

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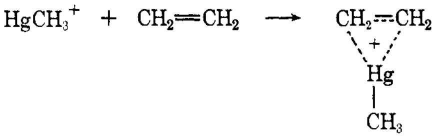
The Observation of a Mercurinium Ion in the Gas Phase by Ion Cyclotron Resonance

Sir:

Mercurinium ions have been postulated as intermediates in the oxymercuration of olefins for many years.[1] However, unequivocal evidence for their involvement has not been reported and Brown[2] has recently discussed the unimportance of mercurinium ions in the oxymercuration of olefins. The first observation of a stable long-lived mercurinium ion was recently reported by Olah and Clifford.[3] They established, on the basis of nmr data, that mercurinium ions are stable in FSO_3H–SbF_5–SO_2 solvent at temperatures below −30°. We now report the first observation of a mercurinium ion in the gas phase.

The ionization of dimethylmercury at 3×10^{-6} Torr in an ion cyclotron resonance (icr) mass spectrometer (Varian Model ICR-9) with 25- and 40-eV electrons and in a cell at room temperature results in 34% Hg^+, 57% CH_3Hg^+, and 9% $CH_3HgCH_3^+$. The spectra were obtained by pulse electron beam modulation to give absorption type signals. When 4×10^{-6} Torr ethylene is added through a second inlet, a new ion is observed corresponding to the mass of $C_2H_4HgCH_3^+$. The new ion is attributed to the ethylene mercurinium ion **1** formed by the reaction shown in eq 1. The six mercury isotopes from 198 to 204 amu are not resolved in the mercury containing ion peaks, but each broad peak is consistent with the mercury isotopic distribution. The ion peak assigned to **1** clearly contains one mercury, three carbons, and 7 ± 2 hydrogens. The intensity of **1** is linearly proportional to the ethylene pressure which is consistent with eq 1. Double resonance experiments[4] performed on $HgCH_3^+$ were inconclusive because there was insufficient resolution between the irradiating and observing frequencies and because the signal-to-noise ratio is small. However, double resonance experiments in which $C_2H_4^+$ was irradiated showed no effect on **1**; this indicates that formation of **1** does not occur by collision of $C_2H_4^+$ with dimethylmercury.



$$HgCH_3^+ + CH_2{=}CH_2 \longrightarrow \underset{\underset{CH_3}{|}}{\overset{CH_2\text{---}CH_2}{\overset{\diagdown\,+\,\diagup}{Hg}}} \qquad (1)$$

1

Under experimental conditions pertaining to the icr experiments, the ion resonance time is about 3×10^{-3} sec. Thus, the ion **1** is clearly stable for this period of time at room temperature. This is so much longer than typical metastable ion lifetimes (~10^{-5} sec) that we regard **1** as a truly stable gas-phase species.

We also wish to report, on the basis of molecular orbital calculations, that the most stable form of this ion is the symmetrically bridged ion **1**. The ion produced upon collision of $HgCH_3^+$ and ethylene could also exist as the unsymmetrical bridged ion **2** or the open classical ion **3**. Prior to Olah's report we had suggested[5] in a molecular orbital study of electrophilic additions to olefins that under suitable conditions mercurinium ions should be capable of independent existence. However, one of the difficulties with postulating the existence of onium ions on the basis of molecular orbital calculations is that the role of solvent in stabilizing charged species is difficult to ascertain. Our icr experiments clearly indicate that mercurinium ions are capable of existence in the absence of solvent.[6]

Extended Hückel[7] molecular orbital calculations were carried out and indicate that the symmetrical ion **1** is 1.9 kcal/mol lower in energy than the unsymmetrical ion **2**.[5] However, the classical ion **3**, with sp^2 hybridization at C_1 and sp^3 hybridization at C_2, is 41 kcal/mol less stable than the bridged ion **1**.[8] Thus, our calculations are in good agreement with experimental nmr evidence[3] where the importance of bridging in mercurinium ions in solution has been established.

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(1) For a recent review of the oxymercuration reaction see W. Kitching, *Organometal. Chem. Rev.*, **3**, 61 (1968).

(2) H. C. Brown and K.-T. Liu, *J. Amer. Chem. Soc.*, **93**, 7335 (1971).

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(5) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

(6) We also have unequivocal evidence that $HgBr_2$ reacts reversibly with an olefin and an allene in the absence of solvent. *trans*-Cyclooctene was passed through a 2-ft 2% $HgBr_2$ on firebrick (no liquid phase was present) gas chromatograph column and was completely (>99.99%) isomerized to *cis*-cyclooctene at 40° (He gas ~ 50 cc/min). The trans olefin was also completely isomerized on a 2.5-ft 5% $HgBr_2$ and 10% SE-30 on firebrick. The trans olefin was 69% isomerized to *cis*-cyclooctene on a 1-ft column. In a control experiment, *trans*-cyclooctene was 1.4% isomerized on a 2.5-ft firebrick column. Optically active 1,2-cyclononadiene, $[\alpha]^{25}D$ −81°, was passed through a 2% $HgBr_2$ on firebrick column and was essentially completely racemized. The same results were obtained with the liquid phase (SE-30) present. These results are only consistent with a reversible equilibrium between the double bond and $HgBr_2$ (unpublished results with R. F. Richter).

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(8) A referee has suggested that rearrangement of **1** to a classical ethyl cation, $CH_3{}^+CHHgCH_3$, should be considered. However, EH calculations suggest that this rearrangement would be endothermic by ~160 kcal/mol. It is also significant that protonation of vinylmercurials in solution does not afford an ethyl cation intermediate.[9] Kinetic studies[10] suggest that an olefin–mercuric halide complex is the product of the rate-determining proton transfer to carbon, rather than a simple carbonium ion.

(9) I. P. Beletskaya, V. I. Karpov, V. A. Moskalenko, and O. A. Reutov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **162**, 414 (1965).

(10) M. M. Kreevoy and R. A. Landholm, *Int. J. Chem. Kinet.*, **1**, 157 (1969).