The seven examples cited here would seem to offer some convincing evidence in support of the mechanism given in eq. 2 for the reaction between NO and vinyl and substituted vinyl radicals at room temperature. Furthermore, starting with the alkyne, reactions 1 and 2 appear to define a new structurally specific route for the scission of carbon–carbon triple bonds.

Further work is in progress in this laboratory on the kinetics of the reactions herein described, on the applicability of the proposed mechanism to alkynyl and vinyl structures in general, and on the properties of the intermediate formed between the vinyl radical and nitric oxide.

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DEPARTMENT OF CHEMISTRY   ALDEN G. SHERWOOD
UNIVERSITY OF ALBERTA   HARRY E. GUNNING
EDMONTON, ALBERTA, CANADA
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Rapid Ligand Exchange in Zirconium(IV) Chelates

Sir:

Several unsuccessful attempts to detect geometric or optical isomers of tetrakis-β-diketone complexes of Zr(IV) and Hf(IV) suggest that in solution rapid ligand exchange is occurring. This hypothesis has been verified by the n.m.r. spectra of mixtures of tetrakis-(2,4-pentanediono)-zirconium(IV), Zr(acac)₄, and tetrakis-(1,1,1-trifluoro-2,4-pentanediono)-zirconium(IV), Zr(tfac)₄.

Zr(acac)₄ and Zr(tfac)₄ were prepared by a previously reported method[1] and were characterized by their melting points and infrared spectra. The n.m.r. spectra were obtained on a Varian Associates Model A-60 spectrometer at 60 Mc. Samples were prepared by weighing the appropriate amounts of Zr(acac)₄ and Zr(tfac)₄ to the nearest 0.0001 g. and then adding benzene to make a 10% solution. Areas of the resonance peaks were measured in mm.² and the total area of the methyl proton resonance was normalized to 4000 mm.². The chemical shifts were measured to ±0.5 c.p.s. relative to benzene.
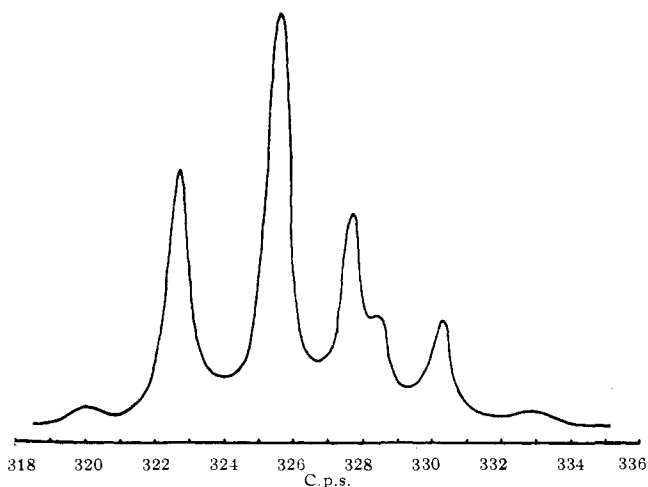

Fig. 1.—The proton n.m.r. spectrum (chemical shift in c.p.s. relative to benzene) of a mixture of Zr(acac)₄ and Zr(tfac)₄; $X = 0.70$.

A benzene solution of Zr(acac)₄ has a methyl resonance at 320.0, the Zr(tfac)₄ at 332.5 c.p.s. Geometric isomers of octahedral complexes containing three un-

(1) E. M. Larsen, G. Terry, and J. Leddy, *J. Am. Chem. Soc.*, **75**, 5107 (1953).
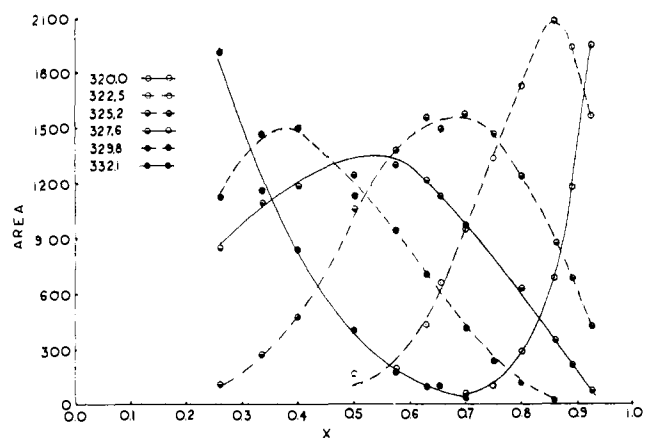

Fig. 2.—The concentration dependence of the methyl resonances.

symmetrical bidentate ligands have been detected by the splitting of the methyl resonance in the n.m.r. spectra.[2,3] With Zr(tfac)₄, rapid ligand exchange makes all the methyl protons equivalent and no splitting is observed. Mixtures of Zr(acac)₄ and Zr(tfac)₄ have methyl resonances at 320.0, 322.5, 325.2, 327.6, 329.8, and 332.1 c.p.s. A typical spectrum is shown in Fig. 1. In several of the spectra the resonances at 325.2 and 327.6 c.p.s. are asymmetric, indicating that two or more peaks are not being resolved. The concentration dependence of the areas of the individual resonances is shown in Fig. 2. Here X represents the mole fraction of the acetylacetonate methyl groups and is equal to $2[\text{acac}]/(2[\text{acac}] + [\text{tfac}])$, where [acac] and [tfac] represent the total number of moles of acetylacetone and trifluoroacetylacetone, respectively.

Because of rapid exchange of the ligands, a solution of Zr(acac)₄ and Zr(tfac)₄ contains the following five compounds: Zr(acac)₄, Zr(acac)₃(tfac), Zr(acac)₂(tfac)₂, Zr(acac)(tfac)₃, and Zr(tfac)₄. For each of the "mixed" compounds, the n.m.r. spectrum is expected to show two methyl resonances, one for the acetylacetone methyl protons and one for the trifluoroacetylacetone methyl protons. Zr(acac)₄ and Zr(tfac)₄ each have one methyl resonance. Thus, eight resonances are expected for the mixture. This is in agreement with experimental results if one assumes that the resonances at 325.2 and 327.6 c.p.s. are unresolved doublets.

For assignment of the resonances, consider the concentration $X = 0.925$. The total concentration of acetylacetone is six times as great as the total concentration of trifluoroacetylacetone; consequently, Zr(acac)₄ and Zr(acac)₃(tfac) are expected to be the most important species in solution. At this concentration the peak at 320.0 c.p.s. is the only resonance which is not decreasing in intensity; therefore, this resonance is assigned to the methyl protons of Zr(acac)₄. The peak of second greatest intensity, at 322.5 c.p.s., is assigned to the acetylacetone methyl protons of Zr(acac)₃(tfac). The intensity of the resonance caused by the trifluoroacetylacetone methyl protons of this compound is one sixth of the intensity of the peak at 322.5 c.p.s. At this concentration, the area of this trifluoroacetylacetone methyl peak is expected to be 260 mm.². The only way of satisfying this is to assume that part of the intensity of the peak at 325.2 c.p.s. is caused by these methyl protons. The remaining area of the peak at 325.2 c.p.s., 160 mm.², is approximately twice the area of the resonance at 327.6 c.p.s.; therefore, the resonance at 325.2 c.p.s. is assigned to the acetylacetone methyl protons of Zr(acac)₂(tfac)₂ and the

(2) R. C. Fay and T. S. Piper, *ibid.*, **84**, 2303 (1962).
(3) R. C. Fay and T. S. Piper, *ibid.*, **85**, 500 (1963).

resonance at 327.6 c.p.s. is assigned to the trifluoro-acetylacetone methyl protons of this compound. By consideration of the other concentration extreme, the remaining resonances can be assigned. The six resonances are assigned as follows: the acetylacetone methyl protons of the compounds $Zr(acac)_4$, $Zr(acac)_3$-$(tfac)$, $Zr(acac)_2(tfac)_2$, and $Zr(acac)(tfac)_3$ resonate at 320.0, 322.5, 325.2, and 327.6 c.p.s. respectively, and the trifluoroacetylacetone methyl protons of the compounds $Zr(acac)_3(tfac)$, $Zr(acac)_2(tfac)_2$, $Zr(acac)$-$(tfac)_3$, and $Zr(tfac)_4$ resonate at 325.2, 327.6, 329.8, and 332.1 c.p.s. This assignment is found to be consistent at all the concentrations studied. Additional evidence for this assignment is found in the small differences in the chemical shift of $Zr(acac)_4$ and $Zr(tfac)_4$ in the mixtures and in pure solutions. However, any argument based on values of the chemical shift is subject to question due to the large concentration dependence of the chemical shift for compounds in benzene solution.[4] The order of the resonances is intuitively satisfactory, since, if substitution of trifluoroacetylacetone for acetylacetone causes a shift in the resonance, one would expect a similar shift in the same direction with additional substitution. This is found to be true in all cases.

At $X = 0.70$, all five compounds are present in sufficient concentrations to allow calculation of the equilibrium constant. For the reaction $3Zr(acac)_4 + 3Zr(tfac)_4 \rightleftharpoons 2\ Zr(acac)_3(tfac) + 2Zr(acac)_2(tfac)_2 + 2Zr(acac)(tfac)_3$, K_{eq} is 1.0×10^8. The high value of K_{eq} reflects the low concentrations of $Zr(acac)_4$ and $Zr(tfac)_4$ in the mixture. At $X = 0.70$, $Zr(acac)_4$ and $Zr(tfac)_4$ account for less than 3% of the species in solution.

Similar exchange has been observed for mixtures of $Hf(acac)_4$ and $Hf(tfac)_4$, $Hf(acac)_4$ and $Zr(tfac)_4$, $Zr(acac)_4$, and $Zr(dbm)_4$, and $Zr(tfac)_4$ and $Zr(dbm)_4$, where dbm represents dibenzoylmethane. These systems are presently being studied in more detail.

Acknowledgment.—This work was performed on apparatus purchased on an N.S.F. equipment grant.

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw–Hill Book Company, Inc., New York, N. Y., 1959, p. 424.

(5) N.S.F. Predoctoral Fellow, 1963–1964.

DEPARTMENT OF CHEMISTRY   A. C. ADAMS[5]
UNIVERSITY OF WISCONSIN   E. M. LARSEN
MADISON 6, WISCONSIN

Lewis Basicity of a Transition Metal. A Boron Trifluoride Adduct of Biscyclopentadienyltungsten Dihydride

Sir:

While transition metals in many complexes are potential Lewis bases (in the sense that they contain nonbonding electron pairs), only a few have appreciable proton affinities,[1] and basicity toward acids other than the proton has never been demonstrated. During studies on the Lewis basicity of certain metal coordinated ligands,[2] we have frequently inspected our data for the possibility of BF_3 coordination with electrons in the d_{z^2}-orbitals of square-planar $Ni(II)$ and $Pd(II)$ complexes (e.g., $Ni(CN)_4^{-2}$, $Pd(SCN)_4^{-2}$, and $Pd(bipy)$-$(NCS)_2$, bipy = 2,2'-bipyridine). We found no evidence for metal basicity in these cases; however,

(1) G. Wilkinson, "Advances in the Chemistry of Co-ordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 50; M. L. H. Green, Angew. Chem., 72, 719 (1960).

(2) D. F. Shriver, J. Am. Chem. Soc., 84, 4610 (1962); ibid., 85, 1405 (1963); A. Luntz and D. F. Shriver, unpublished observations.
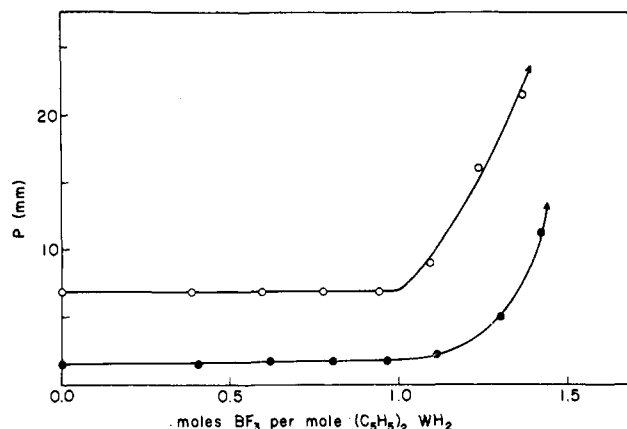

Fig. 1.—The pressure over a toluene solution of $(C_5H_5)_2WH_2$. The abscissa represents moles of boron trifluoride in the condensed phase(s) per mole of $(C_5H_5)_2WH_2$. Closed circles represent data collected at $-22.9°$ and open circles data obtained at $0°$.

recent experiments with $(C_5H_5)_2WH_2$ and BF_3 led to the formation of a 1:1 addition compound which apparently contains a tungsten–boron bond.

The parent $(C_5H_5)_2WH_2$ was prepared by the procedure of Green, *et al.*[3] A melting range of 193 to 195° was observed rather than 163 to 165° as previously reported. This discrepancy is thought to be due to a misprint, since the color, chemical properties, and n.m.r. spectrum agreed with those of the original report and the infrared spectrum was also in substantial agreement. Additional support for the authenticity of this compound was gained from an X-ray powder pattern which was indexed using a slightly larger unit cell and the same space group (C_c) as that reported for $(C_5H_5)_2MoH_2$.[4]
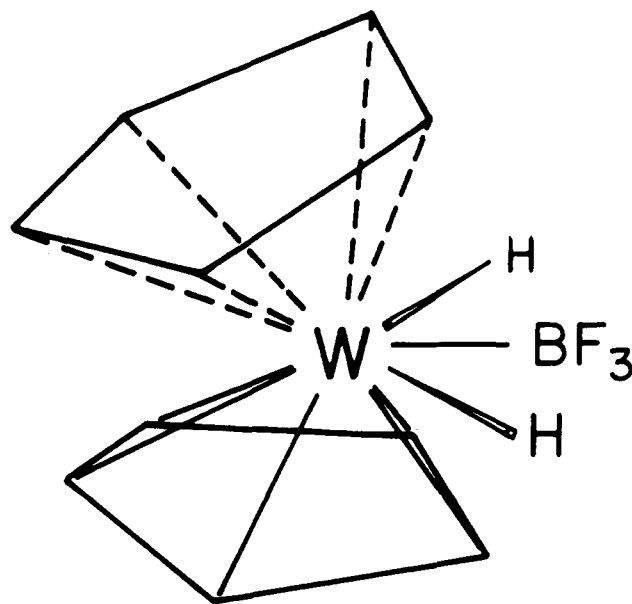

Fig. 2.—The probable molecular geometry of $(C_5H_5)_2WH_2 \cdot BF_3$.

Manipulation of $(C_5H_5)_2WH_2$ and its adduct was performed in either a vacuum line or a nitrogen-filled dry-box. Direct interaction of the cyclopentadienyltungsten hydride with BF_3 led to absorption of 0.954 mole of boron trifluoride per mole of complex. Since this reaction was quite sluggish a tensiometric titration

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

(4) M. J. Bennett, M. Gerlach, J. A. McCleverty, and R. Mason, Proc. Chem. Soc., 357 (1962).