be involved in the advanced stages of nitrogen oxidation. Any more detailed mechanism would be highly speculative before some tracer experiments are carried out.

The yield of oxidized nitrogen ranges between 0.05 and 0.5% calculated on the basis of N_2. If it is calculated, however, on the basis of $^1\Delta_g$ O_2 present in the $OCl^- + H_2O_2$ reaction, which is about 10% of the total O_2*,[19] and taking into account that at least two $^1\Delta_g$ O_2 molecules are required to oxidize N_2 to $2NO_3^-$, one obtains a yield >5% for the $N_2 + {}^1\Delta_g$ O_2 reaction.

The oxidation of N_2 by H_2O_2 induced by catalase deserves a special emphasis. First it confirms the suggestion[20] that catalase or complex I oxidizes H_2O_2 by a double electron transfer, probably by a kind of hydride transfer.[17] Second, it demonstrates that the oxidative action of catalase may be due, at least in part, to the action of singlet excited O_2 molecules. This may be distinctive from the oxidative action of peroxidases.[20] A third point of biochemical interest is the possibility of oxidative nitrogen fixation which may, in spite of the extremely low yields obtained under our experimental conditions, contribute to the nitrogen cycle, in view of the widespread autoxidative processes in nature.

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(20) P. Nicholls and G. R. Schonbaum, *Enzymes*, **8**, 147 (1963).

M. Anbar
The Weizmann Institute of Science
Rehovoth, Israel

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Bis(cyclopentadienyl)zirconium

Sir:

Although there have been several reports relating to efforts to synthesize and characterize bis(cyclopentadienyl)titanium,[1] we are unaware of any attempts to produce the zirconium analog. We report here the synthesis and certain properties of bis(cyclopentadienyl)zirconium; the procedure employed was closely similar to that described previously.[1] The reaction involved is

$$(C_5H_5)_2ZrCl_2 + 2NaC_{10}H_8 \longrightarrow (C_5H_5)_2Zr + 2C_{10}H_8 + 2NaCl$$

In a typical experiment, 12.77 g (43.7 mmoles) of $(C_5H_5)_2ZrCl_2$, 2.01 g (87.4 g-atoms) of Na, *ca.* 12 g of $C_{10}H_8$ (10% molar excess), and 150 ml of tetrahydrofuran (THF) (freshly distilled over sodium benzophenone) were brought together in a 250-ml flask containing dry helium. The anhydrous, oxygen-free atmosphere was maintained while the reaction mixture was stirred for 24 hr. The THF was removed by distillation under reduced pressure and the residue was extracted with benzene which was freshly distilled after having been degassed with dry nitrogen and dried over $LiAlH_4$. Benzene was removed from the resulting dark purple (almost black) solution under reduced pressure. Naphthalene was removed from the solid residue by sublimation for 10 hr at 100° and 10^{-2} mm to provide 8.5 g (88% yield based on Na) of small purple-black, chlorine-free, *pyrophoric* crystals, mp >300° dec. Further removal of the last traces of $C_{10}H_8$ was accomplished by sublimation from small portions of the crude product over 10 hr at 150° and 10^{-3} mm. The importance of maintaining an anhydrous, oxygen-free atmosphere of high integrity throughout all of these operations cannot be overemphasized.

Anal. Calcd for $(C_5H_5)_2Zr$: Zr, 41.2; C, 54.2; H, 4.55. Found: Zr, 40.0; C, 54.2; H, 4.58.

Zirconium was determined by oxidation to ZrO_2 and the results were uniformly low; this is believed due to small but unavoidable losses of the sample in the initial stages of the extremely exothermal oxidation. In contrast to the titanium analog,[1] however, the analytical data for carbon and hydrogen were consistently satisfactory.

Thus far we have been unable to find a solvent in which $(C_5H_5)_2Zr$ is sufficiently soluble to permit a determination of molecular weight; this is a point of particular interest since the titanium analog was found to be dimeric.[1]

Using a modified Curie–Cheneveau balance calibrated with $HgCo(SCN)_4$, $(C_5H_5)_2Zr$ was found to be diamagnetic at 25°; this was confirmed by an esr spectrum of a sample of the solid.

X-Ray diffraction patterns were obtained using Cu $K\alpha$ radiation (Ni filter), 35 kv, 15 ma, and exposure times of 16–20 hr; relative intensities were estimated visually. The *d* spacings (Ångstrom units) and relative intensities (in parentheses) found were: 7.3 (0.3), 5.8 (0.8), 5.2 (0.4), 4.5 (1.0), 4.1 (0.4), 3.5 (0.2), 3.4 (0.2), 3.0 (0.2), 2.5 (0.2), and 1.9 (0.3). Thus it is apparent that $(C_5H_5)_2Zr$ and $(C_5H_5)_2Ti$ are isomorphous.

The infrared spectrum of $(C_5H_5)_2Zr$ (Nujol mulls) included the following bands: 730 (m), 800 (s), 843 (w), 893 (w), 1015 (m), 1042 (w), 1063 (w), 1128 (w), 1165 (w), 1210 (w), and 1262 (w) cm^{-1}; there were no bands in the 2000-cm^{-1} region that could be attributed to Zr–H bonds. In general, the infrared spectrum of this compound was less well resolved than that of the corresponding titanium compound; otherwise the two spectra are closely similar, as expected. Efforts to obtain an nmr spectrum in benzene or toluene failed because of either limited solubility or interference by the solvent.

Bis(cyclopentadienyl)zirconium is appreciably soluble in benzene, toluene, *n*-hexane, and THF at 25°; the solubility in benzene at 5° is very low. When $(C_5H_5)_2Zr$ is heated to 300° at 10^{-3} mm, it turns black and sublimes very slowly; the vapor pressure is qualitatively much lower than that of the titanium analog. The infrared spectrum of the black solid residue was substantially the same as that of the starting material, thus providing no evidence of decomposition.

Air oxidation of $(C_5H_5)_2Zr$ yielded products that varied in both color (yellow to orange) and composition depending upon conditions and rate of reaction. These products were insoluble in a wide variety of solvents, the infrared spectral bands were quite broad, and the

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(1) G. W. Watt, L. J. Baye, and F. O. Drummond, Jr., *J. Am. Chem. Soc.*, **88**, 1138 (1966), and references therein.

X-ray diffraction lines were weak and diffuse. These properties suggest that these oxidation products are polymeric and this is supported by the fact that their infrared spectra were very similar to that of the bis(cyclopentadienyl)titanoxane polymer $[-Ti(C_5H_5)_2-O-]_n$ prepared by Giddings.[2]

Work on the synthesis and characterization of other compounds of the type $(C_5H_5)_2M$, where M is a metal in the 4f or 5f transition series or a lanthanide, is in progress.

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[2] S. A. Giddings, *Inorg. Chem.*, 3, 684 (1964).

George W. Watt, Frank O. Drummond, Jr.
Department of Chemistry, The University of Texas
Austin, Texas 78712
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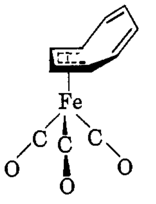
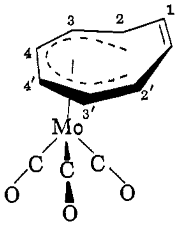
The Crystal Structure of Cyclooctatetraenemolybdenum Tricarbonyl[1]

Sir:

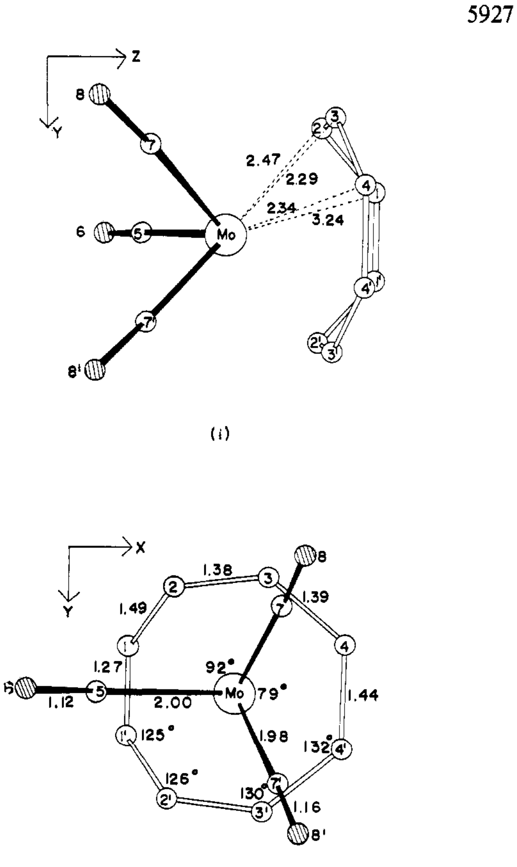
Cyclooctatetraenemolybdenum tricarbonyl, $C_8H_8Mo(CO)_3$ (I),[2] is one of a class of π-bonded cyclic olefin–transition metal complexes where the olefin has more available π electrons than is required by the metal. The possible consequences of this situation on the geometry of the ligand have been examined with particular attention to I, the corresponding cyclooctatetraenechromium tricarbonyl (II), and $C_8H_8Fe(CO)_3$ (III).[3] An nmr investigation[3] of I and II has eliminated the possibility that the "excess" π electrons might be involved in σ bonding resulting in the formation of bicyclic ligands. At 80°, the nmr of I exhibits a sharp singlet, which broadens as the temperature is lowered, and finally, at −30 to −40°, develops a complex multiplet pattern.[2,3] This behavior has been interpreted in terms of a "freezing" of a fixed configuration at lower temperatures, where the metal is involved in bonding with six π electrons, leaving one double bond unaffected. At higher temperatures, valency tautomerism takes place with a rapid rate of interconversion among the tautomers, resulting in all the protons in the molecule becoming equivalent on a time-average basis.[3] We have investigated the crystal structure of I, presupposing that crystal forces are sufficient to "freeze" the lowest energy valence tautomer,[4] in order to examine the molecular geometry of the complex.



III



IV



(i)

(ii)

Figure 1. The complex viewed down (i) the *a* axis, and (ii) the *c* axis. Mo–C distances are ±0.02 A; C–C and C–O distances are ±0.03 A; C–Mo–C angles are ±1°; C–C–C angles are ±2°.

Cyclooctatetraenemolybdenum tricarbonyl crystallizes in the form of thick red plates belonging to the monoclinic system, with $a = 7.33 \pm 0.02$, $b = 10.43 \pm 0.03$, $c = 7.16 \pm 0.02$ A, and $\beta = 107° 15' \pm 20'$, as determined on a precession camera with Mo Kα radiation ($\lambda = 0.7107$ A). There are two molecules of $C_8H_8Mo(CO)_3$ in the unit cell. Systematic absences indicate that the space group is either $P2_1$ or $P2_1/m$. A total of 1046 independent structure amplitudes was obtained by visual estimation of equiinclination Weissenberg photographs (Mo Kα radiation) at 25°. The structure analysis followed the usual heavy atom method,[6] and full-matrix, least-squares refinement incorporating anisotropic temperature factors has given an *R* factor of 0.13 on the 1046 observed reflections.

The molecular structure is shown in Figure 1. Within the accuracy of our analysis, the space group is $P2_1/m$,[7] which requires the molecule to have mirror symmetry with the molybdenum atom and one carbonyl group lying in the reflection plane. The Mo atom is closely, but not equally, associated with C(2), C(3),

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[1] This work was supported in part by the National Institutes of Health (GM 12470-02) and by the Hoffmann-LaRoche Foundation.

[2] S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, 87, 3267 (1965).

[3] C. G. Kreiter, A. Maasbol, F. A. L. Anet, H. D. Kaesz, and S. Winstein, *ibid.*, 88, 3444 (1966).

[4] A recent X-ray study on the geometry of bullvalene, another olefin exhibiting rapid tautomerism, has indicated that at temperatures where rearrangement normally occurs in solution, Ag^+ complexation and crystal forces are sufficient to stabilize one tautomer: M. G. Newton and I. C. Paul, *ibid.*, 88, 3161 (1966). The crystallographic study[5] on cyclooctatetraeneiron tricarbonyl shows no evidence for disorder which would indicate coexistence of valence tautomers in the crystal.

[5] B. Dickens and W. N. Lipscomb, *ibid.*, 83, 4862 (1961); *J. Chem. Phys.*, 37, 2084 (1962).

[6] J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 219 (1937).

[7] After initial attempts to refine the structure in each of the two possible space groups, a decision was made in favor of $P2_1/m$ and the final refinements were based on this group.