the $C_7H_7^+$ reactant, with some preference to the hydrogens originally on the methyl group. The data do not rule out the additional possibility that the fifth ring hydrogen of the neutral toluene scrambles with the $C_7H_7^+$ hydrogens, giving it the possibility of appearing in the product ion with low probability.

The product ion distribution for $C_7H_6D^+$ reacting with $o$-$C_6H_4DCH_3$ indicated that the ring deuterium in the neutral reactant is abstracted with approximately statistical probability (i.e., 20% of the time). Also[19] the $C_7H_7^+$ ion from benzyl bromide (at 13.5 eV) reacted very rapidly with $C_6D_5CH_3$.

The results of these labeling experiments indicate that the identities of the hydrogens in the $C_7H_7^+$ reactant are largely lost, although the preference for transferring the hydrogens originally on the methyl shows that hydrogen scrambling is not complete at these electron energies, and furthermore rule out a fully symmetrical structure for the reacting $C_7H_7^+$ ion. The apparent complete retention of hydrogen identities in the neutral toluene during the reaction suggests that the reaction itself proceeds in a fashion not permitting free atom migrations, and it is reasonable to postulate that the scrambling in $C_7H_7^+$ occurs prior to the reaction, as previous work would also imply.[4,5,8]

Formulating a simple, chemically reasonable mechanism satisfying the observations is apparently possible *only* on the assumption that the reactant $C_7H_7^+$ ion has the benzyl cation structure. Tolyl or tropylium structures must at some point in the reaction be rearranged to the benzyl structure. We postulate that the reaction proceeds as in Scheme II.

**Scheme II**
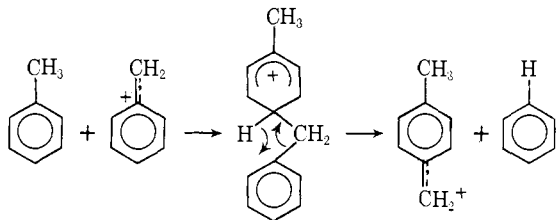


The proposed initial attack (without positional selectivity) on a ring site of the neutral is entirely similar to the mechanism proposed[20] to rationalize the substituent effects in the methylene transfer to aromatic species from $CH_3OCH_2^+$. The evidence seems strong that the reactive $C_7H_7^+$ species has the benzyl structure. Recent photodissociation results[21] indicate that $C_7H_7^+$ formed from toluene has (on a time scale of seconds) two stable, noninterconverting forms, only one of which, presumably the benzyl form, is reactive. We may conclude with some assurance that in the gas phase the benzyl cation exists and is stable for seconds at least and that at least one other isomer (probably the tropylium structure) is also stable for seconds at least.

(19) Benzyl bromide is found by collisional activation to produce 50% benzyl cations at 70 eV (F. W. McLafferty and J. Winkler, private communication) and by analogy with other benzyl derivatives should yield a high fraction of benzyl cation at low energies. It was accordingly chosen as a convenient source of $C_7H_7^+$ cations of probable benzyl structure.

(20) R. C. Dunbar, J. Shen, E. Melby, and G. A. Olah, *J. Amer. Chem. Soc.*, **95**, 7200 (1973).

(21) R. C. Dunbar, unpublished results.

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## Preparation of a Dinitrogen Complex of Bis(pentamethylcyclopentadienyl)zirconium(II). Isolation and Protonation Leading to Stoichiometric Reduction of Dinitrogen to Hydrazine

*Sir:*

In connection with our studies of dinitrogen complexes of group IV transition metal cyclopentadienyls, we have prepared a dinitrogen complex of bis(pentamethylcyclopentadienyl)zirconium(II) *via* the following sequence.

$$ZrCl_4 + 2Li[C_5(CH_3)_5] \longrightarrow (C_5(CH_3)_5)_2ZrCl_2 + 2LiCl \quad (1)$$
$$\mathbf{1}$$

$$2(C_5(CH_3)_5)_2ZrCl_2 + 4Na(Hg) \xrightarrow{N_2}$$
$$\mathbf{1}$$

$$\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3 + 4NaCl \quad (2)$$
$$\mathbf{2}$$
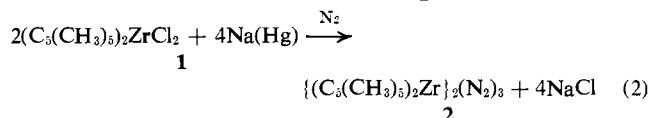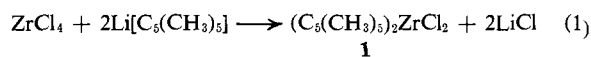
Lithium pentamethylcyclopentadienide is prepared from 1,2,3,4,5-pentamethylcyclopentadiene and *n*-butyllithium in 1,2-dimethoxyethane, then treated *in situ* with freshly sublimed zirconium tetrachloride. Permethylzirconocene dichloride (**1**) is isolated in good yield (50–60%) by a procedure similar to that for the analogous titanium derivative.[1,2] Pale yellow crystalline **1** so obtained analyzes satisfactorily[3] and exhibits a singlet nmr absorption at 1.99 ppm (CDCl₃), nearly identical in position to that observed for permethyltitanocene dichloride.[1]

Reduction of **1** with excess sodium amalgam in toluene under 1 atm of N₂ leads, over the period of 2 days at room temperature, to a dark permanganate-red dinitrogen complex, **2**. **2** is isolated in moderate yields (30–40%) as large, well-formed, metallic *green*[4] crystals by removal of toluene and extraction and subsequent recrystallization from pentane under 1 atm of nitrogen. **2** is moderately soluble in toluene, but only slightly soluble in pentane or diethyl ether. At room temperature in solution, **2** reversibly releases its dinitrogen *in vacuo* over a period of several hours. Quantitative measurements of the N₂ released (eq 3) as well as ele-

$$\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3 \rightleftharpoons 2(C_5(CH_3)_5)_2Zr^6 + 3N_2 \quad (3)$$
$$\mathbf{2} \qquad\qquad\qquad \mathbf{3}$$
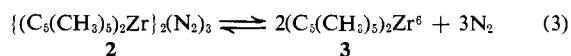
(1) J. E. Bercaw, R. H. Marvich, L. G. Bell, and H. H. Brintzinger, *J. Amer. Chem. Soc.*, **94**, 1219 (1972).

(2) J. E. Bercaw, *J. Amer. Chem. Soc.*, **96**, 5087 (1974).

(3) Calculated for $C_{20}H_{30}Cl_2Zr$: C, 55.56; H, 6.94; Cl, 16.40; Zr, 21.10. Found: C, 55.57; H, 6.99; Cl, 16.36; Zr, 21.21.

(4) The metallic green color of these large crystals appears to be associated with a very high index of refraction. When dissolved in toluene or petroleum ether, even at −80°, dark permanganate-red solutions are observed. Furthermore, the powder obtained by grinding these large green crystals appears red to transmitted but metallic green to reflected light. On the basis of these observations we conclude that the permanganate-red and metallic green compounds are compositionally identical.

mental analyses[5] are in good agreement with the stoichiometry $\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3$.

The molecular weight determined cryoscopically for a solution containing 53.3 mg of **2** per gram of benzene was 820 ± 100, indicating a binuclear solution structure as suggested by its stoichiometry (807 is calculated for **2**). The ${}^1$H nmr spectrum[7] for **2** in toluene-$d_8$ at 25° shows a single, somewhat broadened, resonance centered at $\delta$ 1.75 ppm. Below *ca.* 5° this signal splits into two resonances of nearly equal intensity at 1.74 and 1.76 ppm, indicative of the presence of two isomers of **2** which are in rapid equilibrium on the nmr time scale above this temperature. The full details of this equilibrium are presently under investigation utilizing ${}^{13}$C and ${}^{15}$N nmr and ir spectroscopy and will be reported in a forthcoming paper. The infrared spectrum of **2** (Nujol mull) exhibits, in addition to those bands characteristic of $[\eta\text{-}C_5(CH_3)_5]$ rings, two strong bands at 2041 and 2006 cm$^{-1}$ and a band of medium intensity at 1556 cm$^{-1}$ which shift upon substitution of doubly labeled ${}^{15}N_2$[8] to 1972, 1937, and 1515 cm$^{-1}$, respectively. These three bands are thus attributed to NN stretching frequencies for **2**. The 1556-cm$^{-1}$ band, the position of which suggests a major reduction in the N≡N bond order, could possibly be due to a bridging $N_2$ in a noncentrosymmetric structure, *e.g.*

$$(C_5(CH_3)_5)_2Zr\text{---}N\text{≡}N\text{---}Zr(C_5(CH_3)_5)_2$$

The X-ray crystal structure determination for **2**, in progress at the time of this writing, should settle the questions concerning the mode(s) of Zr–N$_2$ bonding in this dimer.

Treatment of **2** with a 10 *M* excess of HCl at $-80°$ in toluene yields, after subsequent warming to room temperature, a mixture of **1**, $N_2$, $H_2$, $(Zr:N_2:H_2 = 1.000:0.998:0.158)$,[9] and a white crystalline solid identified as pure $N_2H_4\cdot2HCl$.[10] Equation 4 is consequently implicated as a major reaction pathway wherein the four reducing equivalents available in the dimer are utilized in the reduction of 1 of the 3 mol of $N_2$ to $N_2H_4$.

$$\{(C_5(CH_3)_5)_2Zr\}_2(N_2)_3 + 4HCl \longrightarrow$$
$$2(C_5(CH_3)_5)_2ZrCl_2 + 2N_2 + N_2H_4 \quad (4)$$

Chatt, *et al.*, have observed protonation of one of the ligated dinitrogens in complexes of the type *trans*-$[M(Ph_2PCH_2CH_2PPh_2)_2(N_2)_2]$, M = Mo, W; however, the release and/or further reduction of the resulting

(5) Calculated for $C_{20}H_{30}N_3Zr$: C, 59.54; H, 7.44; N, 10.41; Zr, 22.61. Found: C, 59.75; H, 7.36; N, 10.18; Zr, 22.77.

(6) Although **3** has not been completely characterized at present, its nmr spectrum strongly suggests that the predominant species in solution has the structure $(C_5(CH_3)_5)(C_5(CH_3)_4CH_2)ZrH$, apparently formed *via* a *reversible* ring methyl hydrogen abstraction by the Zr center for the tautomer $(\eta\text{-}C_5(CH_3)_5)_2Zr$. A completely analogous tautomeric behavior has recently been established for $(\eta\text{-}C_5(CH_3)_5)_2Ti$ (ref 2).

(7) Spectra were recorded on a Varian HR-220 (CW) spectrometer. ${}^1$H chemical shifts were calculated from their positions relative to the residual aromatic protons in toluene-$d_8$ and converted to values relative to (and downfield of) TMS at $\delta$ 0.

(8) Bio-Rad "${}^{15}N_2$" with a composition (mass spectrum) of ${}^{15}N\equiv{}^{15}N$, 93.3%; ${}^{15}N\equiv{}^{14}N$, 6.3%; ${}^{14}N\equiv{}^{14}N$, 0.37%.

(9) Identical treatment of **3** with HCl yields only **1** and $H_2$ in a 1.00:1.01 mole ratio, respectively.

(10) Isolated *via* extraction of the residue (after removal of toluene) with 6 *M* HCl and identified by its infrared spectrum and a mixture melting point determination.

$[N_2H_2]$ moiety has not been realized.[11] Shilov and coworkers have previously reported the formation of unstable dark blue complexes of the type $[(C_5H_5)_2\text{-}TiR]_2N_2$ and $[(C_5H_5)_2Ti]_2N_2$ on reduction of $(C_5H_5)_2\text{-}TiCl_2$ and $(C_5H_5)_2TiCl$ with RMgX in the presence of $N_2$.[12,13] Protonation under conditions similar to those reported herein produces a near quantitative yield of hydrazine for $[(C_5H_5)_2TiR]_2N_2$ and a mixture of $N_2$ and $N_2H_4$ or $N_2$ and $NH_3$ for $[(C_5H_5)_2Ti]_2N_2$. The exact nature of these dinitrogen complexes is as yet unknown, however.

**2** appears to be the best characterized dinitrogen complex capable of liberating *reduced* $N_2$ on simple protonation and thus represents a first stage of dinitrogen activation well suited for further study. We are presently investigating the essential features of this reaction with respect to whether diimide is an intermediate in hydrazine formation and/or whether the reduction involves a $\mu$-dinitrogen.

(11) J. Chatt, G. A. Heath, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, 1010 (1972).

(12) A. E. Shilov, A. K. Shilova, E. F. Kvashina, and T. A. Vorontsova, *Chem. Commun.*, 1590 (1971).

(13) Y. G. Borodko, I. N. Ivleva, L. M. Kachapina, S. I. Salienko, A. K. Shilova, and A. E. Shilov, *J. Chem. Soc., Chem. Commun.*, 1178 (1972).

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## Solvent Effects on Thioxanthone Fluorescence

*Sir:*

Thioxanthone, **1**, is a commonly used triplet sensitizer,[1] with a lowest $\pi,\pi^*$ triplet at 65.5 kcal/mol.[2]

**1**

While using thioxanthone as a triplet sensitizer in alcohols, we have noted strong luminescence visible to the eye. We wish to report an investigation of this phenomenon which demonstrates that the quantum yield of fluorescence of thioxanthone varies by more than three orders of magnitude as a function of solvent and suggests that caution should be exercised in using thioxanthone as a triplet sensitizer in alcoholic solvents.[3]

Broad structureless fluorescence is observed from solutions of thioxanthone in all solvents used.[4] The rela-

(1) See, for example, (a) G. S. Hammond, *et al., J. Amer. Chem. Soc.*, **86**, 3197 (1964); (b) D. Valentine, Jr., and G. S. Hammond, *ibid.*, **94**, 3449 (1972); (c) S. Hosaka and S. Wakamatsu, *Tetrahedron Lett.*, 219 (1968); (d) O. L. Chapman and G. Wampfler, *J. Amer. Chem. Soc.*, **91**, 5390 (1969); (e) C. D. DeBoer and R. H. Schlessinger, *J. Amer. Chem. Soc.*, **94**, 655 (1972); (f) R. W. Yip, A. G. Szabo, and P. K. Tolg, *J. Amer. Chem. Soc.*, **95**, 4471 (1973).

(2) W. G. Herkstroeter, A. A. Lamola, and G. S. Hammond, *J. Amer. Chem. Soc.*, **86**, 4537 (1964).

(3) Caution should also be exercised at high thioxanthone concentrations because of self quenching. See ref 1d–f.

(4) A few reports of thioxanthone fluorescence have appeared previously. See (a) E. Sawicki, T. W. Stanley, W. C. Elbert, and M. Morgan, *Talanta*, **12**, 605 (1965); (b) H.-D. Dell, J. Fiedler, and R. Kamp, *Z. Anal. Chem.*, **253**, 357 (1971).