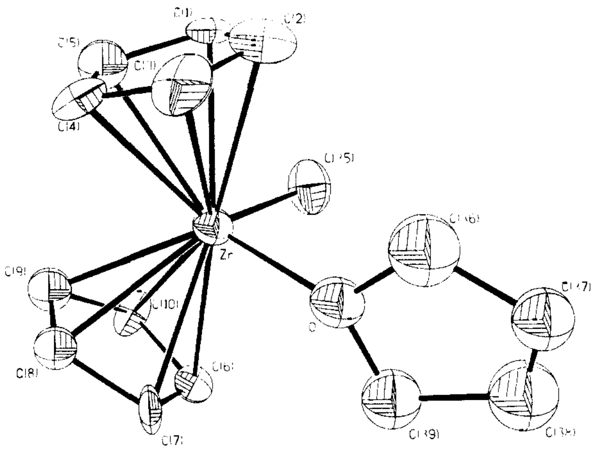

Figure 1. Structure of the $Cp_2Zr(CH_3)(THF)^+$ cation. The BPh_4^- structure is normal. Important bond lengths (Å) and bond angles (deg) are as follows: Zr–C(35) 2.256 (10); Zr–O 2.122 (14); Zr–Cp(av) 2.487 (41); Zr-CNT(av) 2.174; O–C(36) 1.443 (27); O–C(39) 1.464 (25); CNT-Zr-CNT 129.6; C(35)–Zr–O 97.4 (5); C(39)–O–C(36) 104.5 (16); CNT indicates the centroid of a Cp ring.

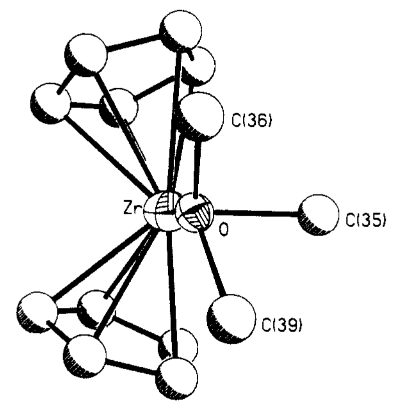

Figure 2. Structure of the $Cp_2Zr(CH_3)(THF)^+$ cation viewed down the O–Zr bond. The β-carbons of the THF ligand have been removed for clarity.

$Cp_2Yb(CH_3)(THF)$ (**4**), in which steric effects should dominate directional bonding effects, the THF ligand lies nearly in the Me–Yb–O plane (dihedral angle = 16°).[16] This difference suggests that there is a significant π component in the Zr–O bond of **3**.[17] Consistent with this proposal, after correction for metal size difference,[18] the M–CH_3 and average M–Cp distances in **3** are ca. 0.04 Å greater than in **4**, while the M–O distance in **3** in ca. 0.04 Å shorter than in **4**.[19-22]

In CH_2Cl_2 solvent, cationic complex **3** is an ethylene polymerization catalyst, producing linear polyethylene with a minimum activity of ca. 0.2 g/(mmol of catalyst) min atm at 25 °C and 1–4 atm of ethylene.[23] This activity is relatively low[11] due to the presence of the THF ligand which, though labile, competes with ethylene for the Zr coordination site. Addition of THF or other donor ligands slows the polymerization rate dramatically and in THF or CH_3CN solvents no activity is observed.[24]

The observation of ethylene polymerization by **3** supports the original Long–Breslow–Newburg mechanism for olefin polymerization by the soluble Ziegler–Natta systems. It also satisfies a necessary condition of the proposal[3] that cationic complex **2** is the active species; i.e., that $Cp_2M^{IV}R^+$ complexes prepared in the absence of Al cocatalysts should polymerize ethylene. Detailed spectroscopic studies of this and related systems are in progress.

Acknowledgment. Support from the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Washington State University Research and Arts Committee is gratefully acknowledged. The X-ray diffraction system was acquired with the aid of NSF grant CHE8408407 and the Boeing Co.

Supplementary Material Available: Summary of X-ray data collection parameters; ORTEP diagram of BPh_4^-; stereoview of $[Cp_2Zr(CH_3)(THF)][BPh_4]$; and tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H atom coordinates and isotropic thermal parameters (11 pages); tables of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[16] Evans, W. J.; Dominguez, R.; Hanusa, T. P. *Organometallics* **1986**, *5*, 263.

[17] In this orientation the THF O p orbital can overlap with the $1a_1$ Zr LUMO. Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729 and references therein.

[18] Yb^{3+} is ca. 0.146 Å larger than Zr^{4+}. Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *A32*, 751.

[19] (a) Other structural comparisons support the proposed Zr–O π-bonding in **3**. The Zr–O bond of **3** is ca. 0.09 Å shorter than the Zr–O bond of $Cp_2Zr(\eta^2\text{-}CPh_2OCH_3)Cl$[19b] and 0.26 Å shorter (after correction for the difference in O and N radii) than the Zr–N bond of $(C_5Me_5)_2Zr$(pyridine)$(C,O\text{-}\eta^2\text{-}OCCH_2)$.[19c] (b) Erker, G.; Dorf, U.; Atwood, J. L.; Hunter, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 2251. (c) Moore, E. J.; Straus, D. A.; Armantrout, J.; Santarsiero, B. D.; Grubbs, R. H.; Bercaw, J. E. *J. Am. Chem. Soc.* **1983**, *105*, 2068.

[20] The chemical significance of Zr–O π-bonding in **3** is under investigation. For example, it provides an explanation[21] for the observation that **3** undergoes hydrogenolysis slowly (2 days) under conditions (1 atm of H_2, room temperature) where the analogous PMe_3 complex $Cp_2Zr(CH_3)(PMe_3)^+$ undergoes instantaneous reaction.[22]

[21] Gell, K. I.; Posin, B.; Schwartz, J.; Williams, G. M. *J. Am. Chem. Soc.* **1982**, *104*, 1846.

[22] Jordan, R. F.; Bajgur, C. S.; Dasher, W. E.; Scott, B.; Rheingold, A. L., submitted for publication in *Organometallics*.

[23] Typical analysis for polymer produced under these conditions: $M_w = 18\,400$; $M_z = 33\,000$; $M_w/M_n = 2.58$.

[24] The THF-free species $Cp_2Zr(CH_3)^+$ (**5**) (or its CH_2Cl_2 solvate) is generated as a transient intermediate in CH_2Cl_2 solution by reaction of $Cp_2Zr(CH_3)_2$ with $[(C_5H_4Me)_2Fe][BPh_4]$. In the presence of THF, **5** is trapped as **3**, while in the absence of potential ligands it decomposes principally to $Cp_2Zr(CH_3)Cl$. Generation of **5** in the presence of 1 atm of ethylene results in very rapid polymerization. The activity of **5** is considerably greater than that of **3**, confirming the inhibition by THF and indicating that THF is not required for polymerization activity. Activity measurements for **5** and polymer characterization are in progress. Jordan, R. F.; Bajgur, C. S.; Echols, S. F., unpublished results.

The Trimethylphosphine Adduct of the Zirconocene–Benzyne Complex: Synthesis, Reactions, and X-ray Crystal Structure

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Although several η^2-benzyne complexes of transition metals have been reported,[2] there are only two examples of mononuclear benzyne complexes which have been structurally characterized. These are the Cp^*TaMe_2(benzyne) ($Cp^* = \eta^5\text{-}C_5Me_5$) complex reported by Schrock[1] and Bennett's 1,2-bis[(dicyclohexylphosphino)ethane]nickel(benzyne) complex.[2] The existence of

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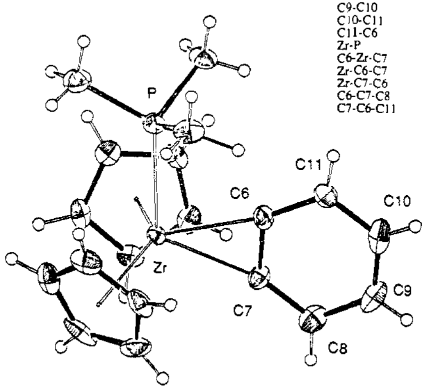
[1] McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.

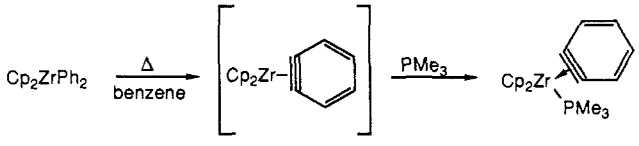
[2] Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992 and references therein.



Zr-C6	2.267(5) (Å)
Zr-C7	2.228(5)
C6-C7	1.364(8)
C7-C8	1.389(8)
C8-C9	1.383(9)
C9-C10	1.380(9)
C10-C11	1.377(9)
C11-C6	1.406(8)
Zr-P	2.687(3)
C6-Zr-C7	35.33(19) (°)
Zr-C6-C7	70.8(3)
Zr-C7-C6	73.9(3)
C6-C7-C8	122.1(5)
C7-C6-C11	120.2(5)

Figure 1. Molecular structure and selected bond lengths and angles of **2**.

Scheme I

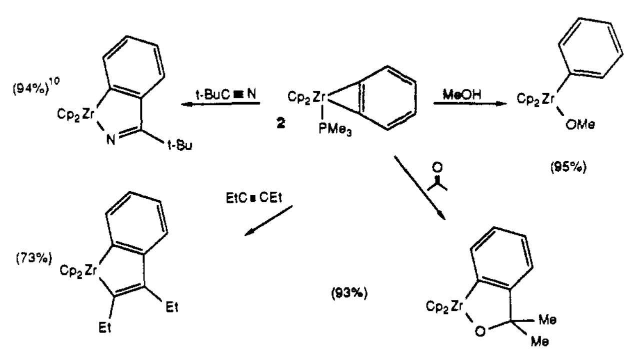


1 **2**

the remainder rests on labelling and trapping experiments.[3,4a] Of these, perhaps the most thoroughly examined is the intermediate complex generated from the thermolysis of diphenylzirconocene (Scheme I) as detailed in the elegant studies of Erker and coworkers.[4] We have been interested in the use of this nascent benzyne complex as a means for carbon–carbon bond formation for use in organic synthesis and have recently reported a study of the trapping of **1** with nitriles to form novel azametallacycles.[5] We now report **1**, when generated in the presence of excess ligand, can be trapped as its trimethylphosphine adduct in good yield.

When diphenylzircononcene is heated to 80 °C in benzene[4] with 10 equiv of trimethylphosphine, ^{1}H NMR reveals the formation of a new cyclopentadienyl resonance at δ 5.28 (C_6D_6).[7] The signal is split by the phosphorus into a doublet, $J_P = 1.9$ Hz. In addition, a new trimethylphosphine resonance is observed at δ 1.01, $J_P = 6.4$ Hz, with a 9:10 ratio of integrals observed for the trimethylphosphine/cyclopentadienyl signals. Complex **2** is formed in ca. 90% yield (by ^{1}H NMR) and the isolated complex has been characterized by ^{1}H, ^{13}C, and ^{31}P NMR, elemental analysis,[7] and X-ray crystallography.

Scheme II



The X-ray crystal structure[8] of **2** is shown in Figure 1. In contrast to Schrock's tantalum complex, no alternation of short and long bond lengths corresponding to "frozen out" single and double bonds is seen. In the present example, all of the C–C bond lengths are identical within experimental error. In this respect, **2** is thus more similar to Bennett's nickel complex[2] than to its closer (in periodicity) tantalum analogue. Interesting, however, is that the C–C "triple bond" length of 1.364 (8) Å is identical with that seen in the tantalum case. It is also worth noting that the Zr–C6 bond is elongated by 0.04 Å as compared to the Zr–C7 bond. This deformation is presumably due to steric crowding by the adjacent trimethylphosphine moiety. That the benzyne moiety of **2** experiences little strain is evident from the fact that the C6–C7 bond length and the C6–C7–C8 and C7–C6–C11 bond angles vary only slightly from that seen in benzene itself.

Although **2** is thermally quite stable, it is also very reactive toward many functional groups. We have just begun to uncover some of its rich reaction chemistry (Scheme II). Thus **2** couples readily with nitriles (as does **1** generated thermally[5]), alkynes,[2,3e,h,9] and ketones and is protonated[2] by methanol to form phenyl zirconocene methoxide.

We are continuing to explore the chemistry of **2** and will report in due course its reactions with other unsaturated species as well as with main-group and transition-metal organometallic compounds. In addition we are studying the preparation of a variety of substituted benzyne complexes as well as trimethylphosphine adducts of zirconocene complexes of a number of strained ring and unstrained acyclic organic systems.

Acknowledgment. The workers at MIT gratefully acknowledge the support of the National Institutes of Health (GM-34917), the Research Corporation, and Alfred Bader. S.L.B. is the recipient of a Distinguished New Faculty Grant from the Camille & Henry

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(7) **Preparation of the Trimethylphosphine Adduct of the Zirconocene–Benzyne Complex.** To a solution of diphenylzirconocene[4a,6] (2.08 g, 5.57 mmol) in benzene (20 mL) under argon was added trimethylphosphine (6.0 mL, 4.41 g, 58.0 mmol) and the resulting solution was heated to 75 °C for 24 h. At this time the benzene and the excess trimethylphosphine were removed in vacuo to yield 2.08 g of a tan powder which was 92% pure by ^{1}H NMR. This corresponds to a 92% yield. An analytical sample was prepared by recrystallization from ether/toluene (60/40): ^{1}H NMR (400 MHz, C_6D_6) δ 1.01 (d, 9 H, $J = 6.4$ Hz), 5.28 (d, 10 H, $J = 1.9$ Hz), 7.47 (m, 2 H), 7.76 (m, 1 H), 8.22 (m, 1 H); ^{13}C{^{1}H}NMR (75.4 MHz, C_6D_6) δ 17.67 (d, $J = 18.8$ Hz), 103.3, 127.8, 128.5, 132.9, 135.0, 154.1 (d, $J = 30.8$ Hz), 174.3 (d, $J = 13.6$); ^{31}P{^{1}H} NMR (121.4 MHz, C_6D_6, referenced to external 85% H_3PO_4) δ -3.916. Anal. Calcd for $C_{19}H_{23}PZr$: C, 61.08; H, 6.20. Found: C, 60.87; H, 6.32.

(8) **Crystallography.** X-ray data were collected at -155 °C using Mo Kα radiation. A total of 1708 reflections were collected in the range $6° < 2\theta < 45°$ with the 1243 having $F > 3\sigma(F)$ being used in the structure refinement which was carried out using a combination of direct methods (MULTAN78) and Fourier techniques. Final $R(F) = 0.0233$ and $R_w(F) = 0.0250$. The positions of all hydrogen atoms were clearly visible in a difference Fourier phased on the non-hydrogen atoms, and the coordinates and isotropic thermal parameters for hydrogens were varied in the final cycles of refinement. Isotropic values for those atoms refined anisotropically are calculated from the formula given by W. C. Hamilton. (*Acta Crystallogr.* **1959**, *12*, 609). Although the molecule possesses near *m* symmetry, it is chiral in this space group. When the enantiomer of the reported structure was refined, the residuals increased significantly $R(F) = 0.033$, indicating that the reported coordinates represent the absolute configuration for the molecule in the crystal studied. The largest peak on the final difference Fourier was 0.3 e/Å^3. **Crystal data**: $a = 14.528$ (5) Å, $b = 8.546$ (2) Å, $c = 13.904$ (4) Å, $V = 1726.27$ Å^3, space group = $P2_12_12_1$, $Z = 4$, mol wt = 373.58 g, ρ(calcd) = 1.437 g cm^{-3}, $\mu = 7.092$ cm^{-1}. An absorption correction was not applied since a ψ scan of several reflections near $\chi = 90°$ indicated that no absorption correction was necessary.

(9) There are a number of examples of group 4 metallocenes inducing reductive coupling of two alkynes; Cf.: Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6422 and references therein.

(10) Yields were determined by ^{1}H NMR.

Dreyfus Foundation, Inc., which he gratefully acknowledges. J.C.H. thanks the Marshall H. Wrubel Computing Center for a generous gift of computing time.

Supplementary Material Available: Listings of final positional and thermal parameters, bond distances and angles, and NMR data for the compounds shown in Scheme II (7 pages); structure factor table for **2** (4 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and Charge Distribution of Bis(4-*tert*-butylpyridine)-bis(3,5-di-*tert*-butylquinone)ruthenium

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Received November 4, 1985

Metal-ligand electron transfer occurs as a fundamental step in redox processes of complexed metal ions, but only in rare cases has it been studied directly. Intramolecular charge separation induced photochemically contributes to the activity of photocatalysts where oxidative and reductive centers result from transfer of charge between localized metal and ligand electronic levels. Ruthenium bipyridine and diimine complexes have been of particular interest in this context[5] and recent studies on *o*-quinone complexes indicate even more facile electron-transfer properties.[6] Quinone ligands[7] chelated to metal ions as either semiquinone or catecholate form complexes with quinone π^* electronic levels and metal d-orbitals close in energy yet discrete in the molecular orbital structure of the complex.[8] This has permitted studies on parameters which direct charge distribution within the metal-quinone chelate ring.[9]

Air oxidation of Ru(bpy)$_2$(DBCat) yields the Ru^{II}(bpy)$_2$(DBSq)$^+$ cation with oxidation occuring at the catecholate ligand.[10] This charge distribution has been determined from the structural features of the cation[11] and from electronic spectroscopic considerations.[10] Complexes containing two quinone ligands bonded to ruthenium were prepared by treating Ru$_2$(OAc)$_4$Cl with DBCat. Addition of excess 4-*tert*-butylpyridine gave Ru(*t*-Bupy)$_2$(DBQ)$_2$.[12] The results of a crystallographic molecular structure determination on the complex show the quinone ligands are bonded strongly to the metal in the trans structure of the molecule (Figure 1).[13] Ruthenium-oxygen bond lengths in this structure are 0.05 Å shorter than values found[11] for Ru(bpy)$_2$(DBSq)$^+$ but are 0.02 Å longer than the 1.974 (4) Å length reported for *trans*-dichlorobis(triazene 1-oxidato)ruthenium(IV).[14] Quinone C-O lengths of the structure are intermediate between values expected for a semiquinone ligand, 1.29 Å, and a catecholate, 1.34 Å. The equivalence of the two quinone ligands and the absence of anisotropy in the oxygen thermal ellipsoids provide evidence that the two quinone ligands are of the same charge, i.e., (DBCat)^2 or (DBSq)$_2$, and not of mixed charge, (DBCat)(DBSq). Moreover, such mixed valence systems commonly show very broad, relatively weak, near-infrared absorptions,[6a,15] not evident here.

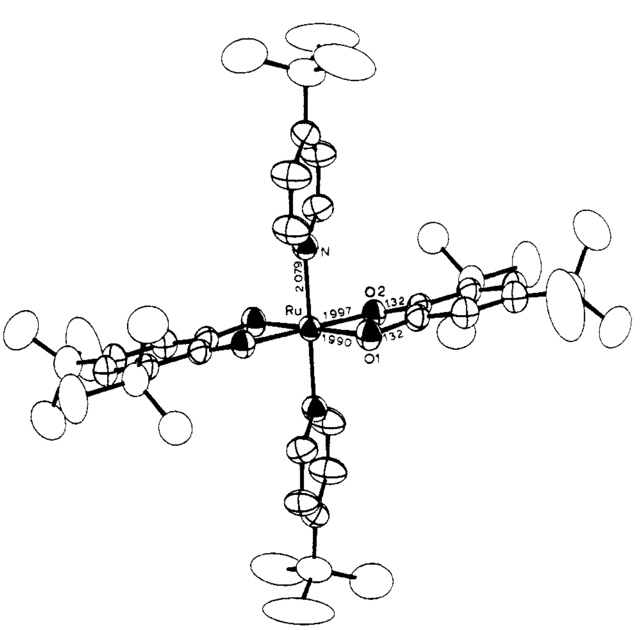

Figure 1. ORTEP plot of the centrosymmetric Ru(*t*-Bupy)$_2$(DBQ)$_2$ molecule. Standard deviations on Ru-O and Ru-N bond lengths are 0.003 and 0.005 Å on C-O lengths.

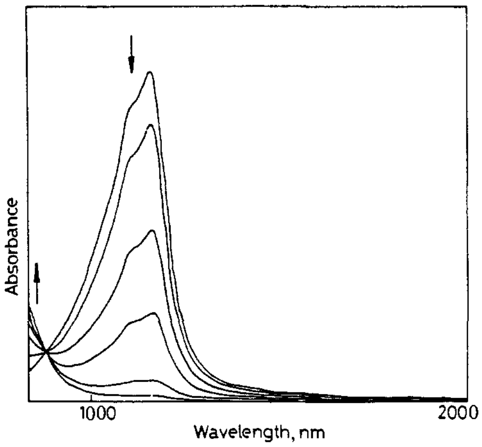

Figure 2. Near-infrared spectrum of Ru(*t*-Bupy)$_2$(DBQ)$_2$ showing absorptions in the 1100-nm region and disappearance of these absorptions upon coulometric oxidation of the complex.

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[1] Current address: Department of Chemistry, Mie University, 1515 Kamihama, Tsu 514, Mie, Japan.

[2] Current address: Department of Chemistry, University College, Singleton Park, Great Britain SA2 8PP.

[3] York University.

[4] University of Colorado.

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[11] Boone, S. R.; Pierpont, C. G.; manuscript in preparation.

[12] Liu, W.; Nevin, W. A.; Haga, M.-A.; Dodsworth, E. S.; Melnik, M.; Lever, A. B. P. to be submitted to *Inorg. Chem.*

[13] Triclinic, $P\bar{1}$, a = 9.072 (2) Å, b = 11.068 (2) Å, c = 11.554 (2) Å, α = 90.25 (2)°, β = 99.51 (2)°, γ = 95.96 (2)°, V = 1137.7 (3) Å^3 at 297 K, D_{calcd} = 1.185 g cm^{-3}, D_{exptl} = 1.17 (2) g cm^{-3}, Z = 1, R = 0.048, R_w = 0.059 for 3918 observed reflections ($F > 6\sigma(F)$).

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