hydride $[(Cy_3P)_2Rh(H)_2Cl]$ (**2**).[15]

The equilibrium of **1** with **2** (eq 1)[15] can be shifted to the dihydride by the addition of base.[16] Even water is able

$$\underset{1}{L_2Rh(H)Cl_2} + H_2 \rightleftharpoons \underset{2}{L_2Rh(H)_2Cl} + HCl \tag{1}$$

$$L = Cy_3P$$

to remove HCl from a low-polar organic phase. The monohydride **1** exhibits low catalytic activity, while the dihydride **2** is isostructural and is isoelectronic with $[(Ph_3P)_2Rh(H)_2Cl]$, which was shown to be an active catalyst in olefin hydrogenation catalyzed by Wilkinson's complex.[2,17] The absence of any additional phosphine ligands in the present system increases the catalytic activity. On the other hand, bulky tricyclohexylphosphine ligands probably decrease the ability of **2** to decarbonylate aldehydes. In contrast to **2**,[18] monohydride **1** is air-stable and very easy to prepare and use.[13]

In conclusion, complex **1** in the presence of H_2O with or without a base is an efficient catalyst (usually 100/1 ratio of substrate/catalyst) for the highly selective hydrogenation of carbon–carbon double bonds in unsaturated carbonyl compounds, including aldehydes.[19]

---

[15] Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *175*, 19.

[16] Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.

[17] Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

[18] Van Gaal, H. M. L.; Verbaak, J. M. J.; Posno, T. *Inorg. Chim. Acta* **1977**, *23*, 43.

[19] General procedure for the hydrogenation of unsaturated carbonyl compounds: the substrate and an organic/aqueous two-phase system (see Table I for specifics) was placed in a 150-mL Schlenk tube. The monohydride **1** was added, and the mixture was immediately degassed by two freeze–pump–thaw cycles. The Schlenk tube was purged with H_2, and the reaction mixture was stirred under H_2 (see Table I for reaction temperature and time). The organic phase was analysed by GC with an internal standard and by GC–MS. Workup (e.g., 4-phenyl-2-butanone) was effected by separation and concentration. The resulting oil was treated with pentane and then percolated through silica or alumina to give pure product.

Stabilization of Dibenzo-*p*-quinodimethane by (Pentamethylcyclopentadienyl)ruthenium Cation

Daniel T. Glatzhofer,* Yongwu Liang, and Masood A. Khan

Department of Chemistry and Biochemistry, The University of Oklahoma, Norman, Oklahoma 73019-0370

Paul J. Fagan

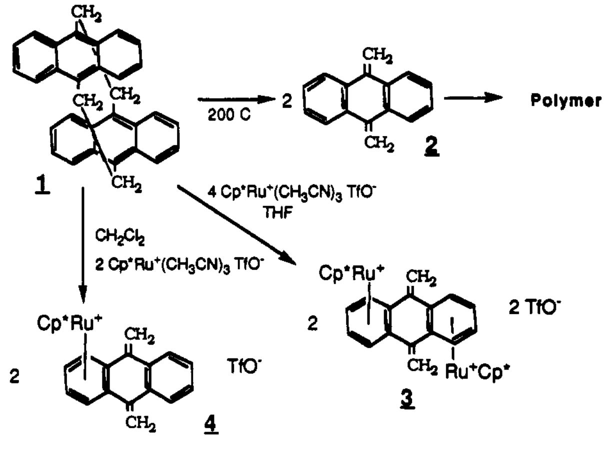
Central Research and Development, E. I. du Pont de Nemours and Co.,
P.O. Box 80328, Wilmington, Delaware 19880-0328

Received February 6, 1991

Summary: Reaction of [2.2]anthracenophane (**1**) with $[Cp^*Ru(CH_3CN)_3]^+CF_3SO_3^-$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl) results in cleavage of the ethano bridges to form stable complexes (*trans*-$[(Cp^*Ru)_2(\eta^6{:}\eta^6$-dibenzo-*p*-quinodimethane$)]^{2+}(CF_3SO_3^-)_2$ (**3**) and $[(Cp^*Ru)(\eta^6$-dibenzo-*p*-quinodimethane$)]^+CF_3SO_3^-$ (**4**)) of the highly reactive dibenzo-*p*-quinodimethane (**2**). An X-ray structural analysis of **3** shows the dibenzo-*p*-quinodimethane moiety to be in a boat conformation.

The use of organometallic groups to stabilize otherwise highly reactive organic species has received considerable attention, with the stabilization of cyclobutadiene by iron tricarbonyl ligands being perhaps the paradigm.[1] Molecular orbital calculations show that quinodimethanes have unusually high free valence at the terminal methylene carbons[2] and are consequently highly reactive species that rapidly dimerize or polymerize when generated under normal conditions.[3-5] Several *o*-quinodimethane and similar species stabilized with iron,[6,7] cobalt,[8] and ruthenium[9-12] moieties have been isolated and characterized, but the stabilization of *p*-quinodimethane species presents a particular challenge. Only one type of metal-stabilized *p*-quinodimethane has been reported (two bis(tricarbonyliron) *p*-quinodimethanes), and synthetic yields were very low (<3.5%).[13] [2.2](9,10)-Anthracenophane (**1**) is known to cleave at moderately high temperatures (100–200 °C)[4] to form dibenzo-*p*-quinodimethane (**2**),

Scheme I



---

[1] Emerson, G. F.; Watts, L.; Pettit, R. *J. Am. Chem. Soc.* **1965**, *87*, 131–133.

[2] Coulson, C. A.; Streitwieser, A. *Dictionary of π-Electron Calculations*; W. H. Freeman: San Francisco, 1965; pp 103–120.

[3] Vögtle, F.; Neumann, P. *Synthesis* **1973**, 85–103.

[4] Golden, J. H. *J. Chem. Soc.* **1961**, 3741–3748.

[5] Errede, L. A.; Szwarc, M. *Q. Rev., Chem. Soc.* **1958**, *12*, 301–320.

[6] Grosselin, J.-M.; Le Bozec, H.; Moinet, C.; Toupet, L.; Dixneuf, P. H. *J. Am. Chem. Soc.* **1985**, *107*, 2809–2811.

[7] Johnson, B. F. G.; Lewis, J.; Thompson, D. J. *Tetrahedron Lett.* **1974**, *43*, 3789–3792.

[8] Hersch, W. H.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1983**, *105*, 5834–5846.

[9] Simpson, N. J.; Cole-Hamilton, D. J. *Polyhedron* **1988**, *7*, 1945–1951.

[10] Bennet, M. A.; McMahon, I. J.; Turney, T. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 379.

[11] Hull, J. W.; Gladfelter, W. L. *Organometallics* **1982**, *1*, 1716–1718.

[12] Chappell, S. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1982**, 1867–1871.

[13] Koray, A. R.; Krieger, C.; Staab, H. A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 521–522.

0276-7333/91/2310-0833$02.50/0

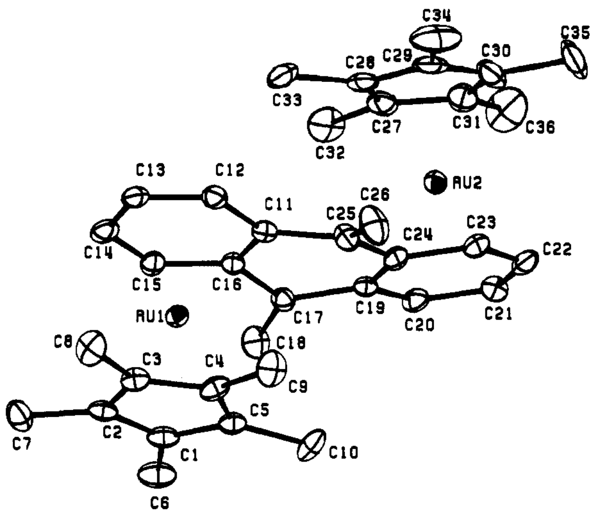


Figure 1. ORTEP drawing of 3. Hydrogen atoms, solvent molecules, and triflate counterions have been omitted for clarity.

which has been characterized in the dilute gaseous phase (Scheme I).[14] We report here a novel reaction in which treatment of 1 with $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$, $TfO^- = CF_3SO_3^-$)[15] results in cleavage of the ethano bridges under mild conditions to generate dibenzo-*p*-quinodimethane complexes 3 and 4 in high yield (Scheme I), which are stabilized by Cp^*Ru^+ groups.

Reaction of 1 with 4 equiv of $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ gives 3 in essentially quantitative yield.[16] Although 1 is not very soluble, the reaction is conveniently monitored by the disappearance of its red-orange color. Compound 3 is remarkably stable, and solutions or crystals can be left in air indefinitely without reaction. Treatment of 1 with 2 equiv of $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ gives the monoruthenium species 4 as an orange solid (90%).[17] Although fairly stable in the solid state, solutions of 4 are highly reactive in air. ^1H NMR and IR spectra[16,17] for 3 and 4 are consistent with the proposed structures, and the NMR data clearly show shielding effects from the Cp^*Ru^+ groups.[15]

Although it is unlikely that the Cp^*Ru^+ groups in 3 would adopt a cis arrangement about the dibenzo-*p*-quinodimethane moiety due to their steric bulk,[15] a single-crystal X-ray structure determination was carried out to unambiguously confirm this.[18] An ORTEP drawing of 3 is shown in Figure 1. The Cp^*Ru^+ groups are clearly trans to one another, and the bond angles and lengths of the dibenzo-*p*-quinodimethane moiety are consistent with the proposed structure. Of particular interest, the bond lengths of the *exo*-methylene groups were found to be 1.325 and 1.323 (6) Å, values typical for isolated double bonds. Figure 1 also shows that the dibenzo-*p*-quinodimethane moiety in 3 is not planar, with C_{15}–C_{16}–C_{17}–C_{18}, C_{18}–C_{17}–C_{19}–C_{20}, C_{12}–C_{11}–C_{25}–C_{26}, and C_{23}–C_{24}–C_{25}–C_{26} torsional angles of 9.4 (5), 17.7 (5), 13.3 (5), and 16.7 (5)°, respectively. This is in accord with MNDO calculations on 2, which predict a boat geometry,[19] and a study on 1,4,5,8-tetraphenyldibenzo-*p*-quinodimethane (5), in which a measured dipole moment of 0.44 D led the authors to conclude that 5 adopts a boat geometry.[20]

The stability of 3 and 4 likely originates from a combination of steric and electronic effects. The stability of 5 and 1,4-diphenyldibenzo-*p*-quinodimethane (6) has been postulated to arise from steric hindrance of the *exo*-methylene groups by the orthogonal phenyl substituents,[20] and it is likely that such effects operate here, especially for 3. However, unlike 5 and 6, one side of 4 is completely nonhindered. It would seem likely, then, that the Cp^*Ru^+ groups also act as electron-withdrawing groups, localizing the electrons of the outer benzo rings as η^6 ligands and isolating the exocyclic double bonds somewhat, as is found in the molecular structure of 4.

The mechanism of ring cleavage of 1 and formation of 3 and 4 under such mild conditions is also of interest, but detailed investigation is complicated by the heterogeneous nature of the reaction. It appears clear that ethano bridge cleavage could occur once two Cp^*Ru^+ groups have attached to 1, but it is unclear whether or not cleavage could be occurring in the process of adding the second Cp^*Ru^+ group or if, after addition of one Cp^*Ru^+ group to 1, the ring cleaves, producing 3 along with 2, which goes on to react further. We have not detected any Cp^*Ru^+ adducts of 1, which seems to favor the latter process. Further investigations of the structure and reactivity of 3 and 4, as well as the mechanism of their formation, are in progress.

Supplementary Material Available: Listings of crystal data, atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for 3 (15 pages); a listing of observed and calculated structure factors for 3 (37 pages). Ordering information is given on any current masthead page.

---

(14) Allan, M.; Heilbronner, E.; Kaupp, K. *Helv. Chim. Acta* **1976**, *59*, 1949–1952.

(15) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698–1719.

(16) Compound 3 was prepared in a drybox under an N_2 atmosphere by adding 4.1 equiv of $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ to a suspension of 2.4 mmol of 1 in 30 mL of dry tetrahydrofuran and stirring the mixture at room temperature for 3 days, at which time the initial dark red-orange solution and solid had faded and a white solid appears. The resulting microcrystalline material was collected by filtration, washed with dry tetrahydrofuran, and dried under reduced pressure to give a nearly quantitative yield of 3. An analytical sample and crystals suitable for X-ray structural determination were obtained by slow diffusion of diethyl ether vapor into a concentrated solution of 3 in nitromethane: mp (CH_3NO_2/Et_2O) 225–227 °C; IR (KBr) $\nu(C{=}CH_2)$ 3085, 1620, 920 cm^{-1}; ^1H NMR (300 MHz, CD_2Cl_2) δ 6.61 (4 H, dd, J = 5.6 and 3.2 Hz), 6.43 (4 H, s), 6.12 (4 H, dd, J = 5.6 and 3.2 Hz), 1.73 (30 H, s). Anal. Calcd for $C_{38}H_{42}F_6O_6S_2Ru_2$: C, 46.81; H, 4.34. Found: C, 46.75; H, 4.40.

(17) Compound 4 was prepared by adding 2.1 equiv of $[Cp^*Ru(CH_3CN)_3]^+TfO^-$ to a suspension of 2.2 mmol of 1 in 60 mL of dry dichloromethane. The flask was fitted with a condensor/gas bubbler, and the mixture was stirred under Ar while it was heated to solvent reflux for 2 days. All other manipulations were carried out in a drybox under an N_2 atmosphere. The resulting solution was filtered and evaporated to give a 91% yield of crude 4, which can be purified by slow diffusion of diethyl ether vapor into a concentrated solution of 4 in nitromethane: mp (CH_3NO_2/Et_2O) >260 °C, reaction occurs; IR (KBr) $\nu(C{=}CH_2)$ 3090, 1615, 925 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (2 H, dd, J = 3.3 and 6.0 Hz), 7.46 (2 H, dd, J = 3.3 and 6.0 Hz), 6.38 (2 H, dd, J = 2.2 and 4.5 Hz), 6.18 (2 H, dd, J = 2.2 and 4.5 Hz), 6.05 (2 H, s), 5.98 (2 H, s), 1.58 (15 H, s). Anal. Calcd for $C_{27}H_{27}F_3O_3SRu$: C, 55.00; H, 4.61. Found: C, 54.97; H, 4.61.

(18) See the supplementary material; a complete discussion of crystallographic details for 3 will be provided in a full paper. Crystal cell data for 3: $C_{40}H_{48}F_6N_2O_{10}S_2Ru_2$; monoclinic, space group $P2_1/n$ (nonstandard setting of $P2_1/c$); a = 12.748 (4), b = 21.858 (7), c = 16.708 (6) Å; β = 105.28 (3)°; V = 4491.0 Å^3; M_r = 1097.08; ρ_{calcd} = 1.622 g cm^{-3}; Z = 4; $F(000)$ = 2224; λ(Mo Kα) = 0.71069 Å; μ = 8.3 cm^{-1}. Cell dimensions and intensities of 8813 reflections were measured at −110 (2) °C ($2\theta_{max}$ = 50°, $\pm h,\pm k,\pm l$) on an Enraf-Nonius CAD-4 diffractometer. The structure was solved by using the heavy-atom method and refined anisotropically by full-matrix least squares (all the hydrogen atoms were located and refined isotropically). All calculations were carried out with use of the SHELX-76 program. For 6186 unique observed reflections ($I > 2\sigma(I)$) the final refinement parameters were R = 0.033, R_w = 0.032, and GOF = 1.15, where $R = \sum(|F_o| - |F_c|)/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, and GOF $= |\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$.

(19) Dewar, M. J. S. *J. Am. Chem. Soc.* **1982**, *104*, 1447–1449.

(20) Dickerman, S. C.; Berg, J. H.; Haase, J. R.; Varma, R. *J. Am. Chem. Soc.* **1967**, *89*, 5457–5458.