porium zizaniae and *Ophiobolus heterostrophus*, *i.e.*, zizanin A, m.p. 121° ($C_{25}H_{38}O_3$), zizanin B,[4] m.p. 173° ($C_{25}H_{38}O_4$), and a compound, m.p. 136° ($C_{25}H_{34}O_3$). The structural relationship between these congeners and the chemical reactions of ophiobolin will be published elsewhere.

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Homogeneous Catalytic Hydrogenation of Ethylene and Acetylene with Four-Coordinated Iridium and Rhodium Complexes. Reversible Catalyst–Substrate Adducts[1]

Sir:

Square-planar carbonyl complexes of univalent iridium[2] and rhodium,[3] *trans*-[MX(CO)(Ph$_3$P)$_2$] (M = Ir, Rh; X = halogen), catalyze reactions of ethylene, propylene, and acetylene with molecular hydrogen in benzene or toluene solutions at subatmospheric pressures of the reacting gases and at relatively mild temperatures (40–60°). Unlike previously reported examples of homogeneous catalytic hydrogenations in solution,[4] these systems *combine* the following important features.

(a) The compositions, properties, and structures[5] of the catalyst complexes are known.[2,3] Their solution chemistry and infrared spectral data (ν_{CO}) indicate that their *trans* square-planar configurations prevail in solution[6,7]; that is to say, the identities of the *actual* catalysts are known with reasonable certainty.

(b) The iridium complexes react *reversibly* with 1 mole of hydrogen per complex.[1b] Equation 1 illustrates the formation of the hydrogen adducts; the two

trans-Ph$_3$P (not shown in the diagram) of [IrX(CO)(Ph$_3$P)$_2$] and [H$_2$IrX(CO)(Ph$_3$P)$_2$] are normal to the plane of the paper (see (c) below). Volumetric measure-

$$(1)$$
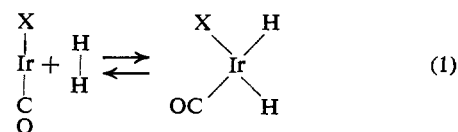
ments of hydrogen absorption (in toluene) indicate that the reaction is first order with respect to the Ir complex. At 20° and a constant pressure of 700 mm. of hydrogen, a practically complete conversion to the dihydride is observed (pseudo-first-order k = 3.2 × 10^{-4} sec.$^{-1}$, [Ir] = 2.3 × 10^{-3} M).[8] At higher temperatures and/or lower hydrogen pressures, the reverse reaction becomes appreciable, and the equilibrium (eq. 1) shifts to the left.

(c) The hydrogen adducts, [H$_2$IrX(CO)(Ph$_3$P)$_2$], have been isolated[9] and characterized,[1b] and the molecular configurations of these catalytic intermediates (*cis*-(H)$_2$–*trans*-(Ph$_3$P)$_2$, see eq. 1) have been established by infrared (crystals and solutions) and n.m.r. (solutions) measurements.[7]

(d) The iridium complexes react *reversibly* with ethylene, acetylene, and other unsaturated substrates at ambient conditions[8] (eq. 2). For example, volumetric

$$(2)$$
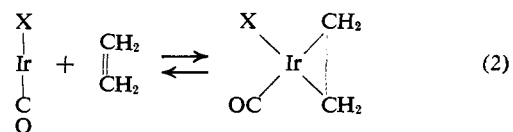
measurements of ethylene absorption by [IrI(CO)(Ph$_3$P)$_2$] in toluene at 26° and 700 mm. of C$_2$H$_4$ (constant) indicate formation of a colorless adduct, assumed to be [(C$_2$H$_4$)IrI(CO)(Ph$_3$P)$_2$] (*ca.* 70% conversion; the chloro complex is less reactive toward ethylene; with acetylene, rather irreproducible results have been obtained thus far). Although the addition compounds have not been isolated owing to their rapid dissociation in the absence of excess substrate, the structure of the ethylene adducts shown in eq. 2 (the two *trans*-Ph$_3$P are normal to the plane of the paper) is assumed by analogy with that of the corresponding oxygen complex, [O$_2$IrCl(CO)(Ph$_3$P)$_2$],[10] and the established orientation of olefins in metal–olefin compounds.[11] A recent report gives evidence for extensive σ bonding in the closely related complex, [(C$_2$F$_4$)IrCl(CO)(Ph$_3$P)$_2$].[12]

The catalytic experiments[13] were carried out by adding the reactants (initially: p_{H_2} 290–620 mm.; p_{alkene} or $_{alkyne}$ 270–440 mm.) to an air-free solution of the complex (1.3–15 × 10^{-3} M), stirring the solution (20–80°, 7–26 hr.), and observing changes of total

(1) (a) Activation of Molecular Hydrogen and Related Molecules by Transition Metal Complexes. II. (b) For part I, see L. Vaska and J. W. DiLuzio, *J. Am. Chem. Soc.*, 84, 679 (1962).

(2) L. Vaska and J. W. DiLuzio, *ibid.*, 83, 2784 (1961).

(3) (a) Prepared by the same method[2] as [IrX(CO)(Ph$_3$P)$_2$]; (b) L. Vallarino, *J. Chem. Soc.*, 2287 (1957).

(4) See, for example, these recent reports (and the references cited therein): (a) F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Ind.* (London), 560 (1965); (b) J. F. Young, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Chem. Commun.* (London), 131 (1965); (c) M. F. Sloan, A. S. Matlack, and D. S. Breslow, *J. Am. Chem. Soc.*, 85, 4014 (1963); (d) R. D. Cramer, E. L. Jenner, R. V. Lindsay, Jr., and U. G. Stolberg, *ibid.*, 85, 1691 (1963); (e) J. Kwiatek, I. L. Mador, and J. K. Seyler, "Reactions of Coordinated Ligands," Advances in Chemistry Series, No. 37, American Chemical Society, Washington, D. C., 1963, p. 201.

(5) The *trans* square-planar structures of the isostructural [MX(CO)(Ph$_3$P)$_2$] (ref. 2) have been confirmed by X-ray studies on [RhCl(CO)(Ph$_3$P)$_2$]: S. F. Watkins, J. M. Obi, and L. F. Dahl, private communication from L. F. Dahl to L. Vaska, 1965.

(6) D. M. Adams, "Spectroscopy," The Institute of Petroleum, London, 1962, p. 265.

(7) L. Vaska, forthcoming publications.

(8) With [RhCl(CO)(Ph$_3$P)$_2$], volumetric measurements have failed to give evidence for hydrogen or ethylene uptake at these conditions.

(9) Pure crystals are colorless; they are best obtained from "concentrated" toluene solutions, [Ir] ≥ 10^{-2} M; oxygen must be rigorously excluded (*cf.* ref. 1b).

(10) (a) L. Vaska, *Science*, 140, 809 (1963); (b) S. J. La Placa and J. A. Ibers, *J. Am. Chem. Soc.*, 87, 2581 (1965).

(11) See, for example, P. R. H. Alderman, P. G. Owston, and J. M. Rowe, *Acta Cryst.*, 13, 149 (1960).

(12) R. Cramer and G. W. Parshall, *J. Am. Chem. Soc.*, 87, 1392 (1965).

(13) Ranges of employed conditions in parentheses.

pressure. Alternatively, the gas mixture was circulated internally through the solution. At the conclusion, gas and solution samples were analyzed chromatographically, and the metal complex was recovered and identified. At 20–30°, only negligible conversions were observed within several hours; at 40°, 12 mole %[14] of ethane was produced from C_2H_4 and H_2 catalyzed by [IrCl(CO)(Ph$_3$P)$_2$] (24 hr.); at 60°, the yield of C_2H_6 was 40% (18 hr.). At the latter conditions, 10% propane was obtained from propylene, and 10 and 5% of C_2H_4 and C_2H_6 were obtained, respectively, from acetylene. With [RhCl(CO)(Ph$_3$P)$_2$], lower conversions were observed (e.g., 24% of C_2H_6 from C_2H_4 at 60°, 22 hr.).[15] The homogeneous hydrogenation of acetylene and ethylene has also been reported for the related rhodium complex [RhCl(Ph$_3$P)$_3$],[4a,16] as well as the platinum–tin system.[4d]

The possible mechanisms of these reactions and some factors determining catalytic hydrogenations with metal complexes will be discussed in a subsequent communication.

(14) The per cent yield refers to the mole per cent of the product in the final gas mixture (consisting of excess reactants, products, and solvent vapor) above the solution in the closed reactor.

(15) At higher temperatures, ≥ 80°, gas circulation over extended periods caused slow reduction of the complexes to metals which rapidly catalyzed hydrogenation of the aromatic solvent. Thus, the absence of these hydrogenated species (e.g., cyclohexane) among the products served as an evidence for the homogeneity of the catalyses reported in this note.

(16) This compound, discovered by us independently several years ago, is highly dissociated in solution, and its composition and structure in solution are unknown at present (cf. (a) in text).

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Cyclohex-2-ene-1,4-dione

Sir:

Although a considerable number of isolable diketo tautomers of di- and higher-substituted hydroquinones are known,[1] the parent compound, cyclohex-2-ene-1,4-dione (1), is unreported. Our curiosity about the conformation and tautomeric stability of 1 prompted its attempted synthesis. In this report, we wish to describe briefly this synthesis and relate some information regarding the stability of 1.

The starting material was hydroquinone (7) which was converted to 4-benzoyloxycyclohexanone (2) in three steps according to a reported procedure.[2] Transformation of 2 to 3 was effected by ketalization followed by saponification. Monobromination of 3 proceeded quantitatively at 40–45° in ethylene glycol containing 25 mole % sulfuric acid to give 4.[3] During

(1) See, for example: G. R. Yoke and co-workers, *J. Org. Chem.*, 24, 1251 (1959); W. Mayer and R. Weiss, *Angew. Chem.*, 68, 680 (1956); A. P. Ter Borg, *Rec. trav. chim.*, 73, 5 (1954), M. Orchin and L. W. Butz, *J. Org. Chem.*, 8, 509 (1943).

(2) E. R. H. Jones and F. Sondheimer, *J. Chem. Soc.*, 615 (1949).

(3) E. W. Garbisch, Jr., *J. Org. Chem.*, 30, 2109 (1965). Excess bromine (10%) was used for the bromination of 3. Brominations in ether led to considerable oxidation of the hydroxyl.

2–3 days at 30°, chromium trioxide–pyridine[4] converted crude 4 to 5, b.p. 77–80° (0.4 mm.), m.p. 39–41°[5]; n.m.r. (in CCl$_4$) τ 5.86 (α-vinyl) and 3.50 (β-vinyl), $J_{\alpha,\beta} = 10.4$ c.p.s. *Anal.* Calcd. for C$_8$H$_{10}$O$_3$: C, 62.33; H, 6.54. Found: C, 62.10; H, 6.34.
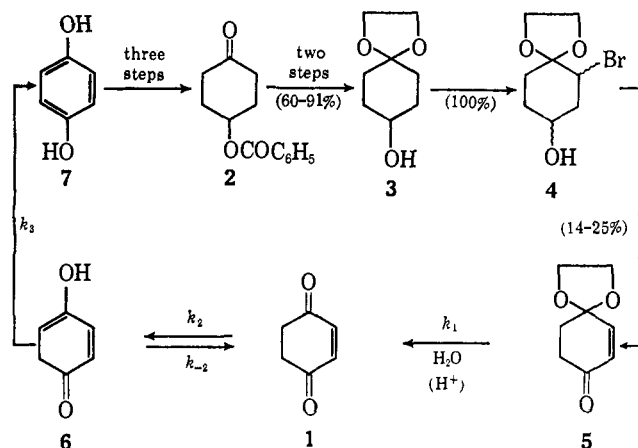
A mixture of one part of 5 and three parts of 0.5 M sulfuric acid (w./v.) was stirred at room temperature until a homogeneous solution resulted; this was left for approximately 30 min. (the reaction may be monitored conveniently by n.m.r.). Extraction of this solution with methylene chloride yielded, after drying the extract and evaporation of the solvent at 1 mm. and 0°, crude 1. Sublimation of the crude product at 0.1 mm. and 25° afforded 20–30% of 1, m.p. 54°; n.m.r.[6] (in CCl$_4$) τ 3.30 (vinyl) and 7.12 (aliphatic) (relative areas 1:2), $J_{\text{vinyl}} = 10.2$ c.p.s. (^{13}C satellite); infrared (in CCl$_4$) ν 1690 (C=O) and 1600 cm.$^{-1}$ (C=C); ultraviolet (in ethanol)[7] λ 233 (ϵ 15,100, $\pi \to \pi^*$) and 352 mμ (ϵ 64, n $\to$ π^*), (in isooctane) λ 219 (ϵ 15,700, $\pi \to \pi^*$) and 365 mμ (ϵ 58, n $\to$ π^*). *Anal.* Calcd. for C$_6$H$_6$O$_2$: C, 65.45; H, 5.49. Found: C, 65.67; H, 5.49.

Crystalline 1 is stable over prolonged periods at 10°. In nonpolar aprotic solvents, tautomerization to 7 is slow, but in aqueous and alcoholic solutions this reaction proceeds rapidly (see below).[7] In trifluoroacetic acid-*d*–deuterium oxide, 5 is converted to 7 with no detectable (<5% by n.m.r.) incorporation of deuterium and no spectroscopic (ultraviolet and n.m.r.) evidence for the intermediacy of 6. Consequently, $k_3 \gg k_{-2}$ and k_2 in the above reaction sequence. First-order rate constants, k_1 and k_2, for the consecutive reactions 5 to 1 and 1 to 6 may be obtained conveniently by n.m.r. (k_1 by following the appearance of ethylene glycol and k_2 by following the appearance of 7 or disappearance of 1). Some results over various sulfuric acid concentrations are given in Table I.

The significant aspects of the data in Table I are the large value of k_1/k_2 which allows the described synthesis and the high rate of enolization of 1 (k_2) in

(4) G. I. Poos, G. E. Arth, R. E. Beyler, and L. H. Sarett, *J. Am. Chem. Soc.*, 75, 422 (1953).

(5) The freshly distilled 5 freezes at 20–25°. Many recrystallizations from ether–pentane with concomitant loss of material are required to raise the melting point to that reported. There appears to be no disadvantage in using crude 5 in the reaction sequence.

(6) Two per cent solution (w./w.). τ values decrease upon increasing concentration.

(7) Approximately 6% of 7 was formed during the time required to prepare the ultraviolet solution and determine the spectrum. The value of ϵ is corrected for this extent of tautomerization.