

solutions) was found to proceed readily over the temperature range 28 to 50°, and the earlier kinetic measurements on this system by Just and Kauko⁴ have been confirmed and extended. The complete rate law was found to be $-d[\text{CO}]/dt = k[\text{CO}][\text{MnO}_4^-]$ with $\Delta H^* = 13$ kcal./mole and $\Delta S^* = -17$ e.u., both substantially constant over the pH range 1 to 13.

A remarkable feature of the latter reaction is its very marked sensitivity to catalysis by Ag^+ and Hg^{2+} (but not Cu^{2+} , Fe^{3+} , Cd^{2+} or Tl^{3+}). The rate law, indicated by preliminary measurements, for the catalytic path in dilute perchloric acid solution is, in each case, $k[\text{CO}][\text{MnO}_4^-][\text{M}]$ where $\text{M} = \text{Ag}^+$ or Hg^{2+} . For Ag^+ , $k(0^\circ) = 1.10 \times 10^5 M^{-2}\text{sec}^{-1}$, $\Delta H^* = 1.2$ kcal./mole and $\Delta S^* = -31$ e.u.; for Hg^{2+} , $k(0^\circ) = 1.06 \times 10^3 M^{-2}\text{sec}^{-1}$, $\Delta H^* = 6.4$ kcal./mole and $\Delta S^* = -21$ e.u. It is suggested that the remarkably high reactivities exhibited by CO in these catalytic reactions are related to favorable oxidation paths involving intermediates such as $[-\text{Hg}-\text{CO}-\text{OMnO}_3]$, analogous to that postulated in the oxidation of CO by Hg^{2+} . It also seems likely that there exists a connection between the Ag^+ -catalyzed oxidation of CO by MnO_4^- in solution and the very efficient oxidation of CO by solid AgMnO_4 .⁵

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- (4) G. Just and Y. Kauko, *Z. physik. Chem.*, **82**, 71 (1913).
 (5) M. Katz, *Advances in Catalysis*, **5**, 177 (1953).
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A TRIHYDRIDO COMPLEX OF IRIDIUM(III)

Sir:

The hydrido complexes $[\text{IrH}_n\text{Cl}_{3-n}(\text{PPh}_3)_3]$ ($n = 1, 2$) have been reported recently.¹ We now wish to describe the preparation and properties of the third member of this series, $[\text{IrH}_3(\text{PPh}_3)_3]$ ($n = 3$) (I). This compound is the first reported example of a transition metal trihydride stabilized by tertiary phosphine ligands.

The yellow complex $[\text{IrHCl}_2(\text{PPh}_3)_3]$ ¹ readily dissolves in a tetrahydrofuran solution of lithium aluminum hydride to give a colorless solution, which, after hydrolysis with water or ethanol and removal of solvent at 12 mm., yields an off-white solid. Extraction with benzene and crystallization from 50% *n*-hexane-cyclohexane mixture affords trihydrido-*tris*-(triphenylphosphine)-iridium(III) as needles (35% yield).

Anal. Calcd. for $\text{C}_{54}\text{H}_{48}\text{IrP}_3$: C, 66.0; H, 4.9; Ir, 19.6; P, 9.5. Found: C, 66.3; H, 4.7; Ir, 19.0; P, 9.5.

The compound is diamagnetic in the solid state, monomeric in benzene solution and has a dipole moment of 4.95 D. Other properties are given in the table.

The deuterido complex corresponding to (I) (similarly prepared from $[\text{IrHCl}_2(\text{PPh}_3)_3]$ and Li-

(1) L. Vaska, *J. Am. Chem. Soc.*, **83**, 756 (1961).

TABLE I

Compound	M.p. (dec. in vacuum)	Color	$\nu_{\text{I-H}}$ (cm. ⁻¹)
(I) $[\text{IrH}_3(\text{PPh}_3)_3]$	227-229°	Colorless	2100, 1745 ^b
(II) $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$	218-220	Colorless	2210, 2130 ^c
(III) $[\text{IrHCl}_2(\text{PPh}_3)_3]$ ^a	261-263	Pale yellow	2230 ^c

^a Crystallizes with a molecule of benzene. ^b Chloroform solution. ^c Halocarbon mull.

AlD_4) shows absorption due to $\nu_{\text{I-D}}$ at 1535 and 1255 cm.⁻¹. The isotopic shift factors are in the range 1.37-1.40 (calculated 1.41).

Two isomeric forms of $[\text{IrH}_3(\text{PPh}_3)_3]$ are possible theoretically, but the presently available data do not allow us to distinguish between them with certainty.

(I) reacts with hydrogen chloride in ether, evolving hydrogen, and affording (II) and (III) with one and two equivalents of acid, respectively; (III) does not react with acid under these conditions. (II) and (III) probably are isomeric with Vaska's compounds¹ and (III) is similar in type to the recently reported hydrido complexes of rhodium and iridium.²

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- (2) J. Chatt and B. Shaw, *Chem. & Ind. (London)*, 931 (1960); J. Lewis, R. Nyholm and G. Reddy, *ibid.*, 1386 (1960).

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UNSATURATED MACROCYCLIC COMPOUNDS. XX.1 SYNTHESIS OF THREE COMPLETELY CONJUGATED TWENTY-MEMBERED RING CYCLIC SYSTEMS

Sir:

We wish to report the synthesis of the completely conjugated twenty-membered ring cyclic systems 1,3,5,7,11,13,15,17-cycloeicosaoctaene-9,19-diyne (II or a stereoisomer), 1,3,5,7,9,11,13,15,17-cycloeicosanonaen-19-yne (VI or a stereoisomer) and 1,3,5,7,9,11,13,15,17,19-cycloeicosadecane (III or a stereoisomer). These compounds, the first examples of monocyclic conjugated 20 π -electron systems, were expected to be non-aromatic since they do not comply with Hückel's rule for aromaticity [presence of $(4n + 2)$ π -electrons].

1,5,9-Decatriyne² on oxidation with cupric acetate in pyridine³ at 55° for 4 hr. yielded (besides other products)² 6% of the colorless cyclic dimer, 1,3,7,11,13,17-cycloeicosahexayne (I) [m.p. 230-231° dec.⁴; $\lambda_{\text{max}}^{\text{isooctane}}$ 226, 238 and 255 μ]; found: C, 93.91; H, 6.24; converted by full hydrogenation to cycloeicosane, m.p. and mixed m.p. 60-61°. Rearrangement of I with potassium *t*-butoxide in *t*-butyl alcohol-benzene at 90° for 15 minutes yielded ca. 30% of an isomer (found: C, 93.03; H, 5.95) as dark brown-violet

(1) Part XIX, F. Sondheimer, R. Wolovsky and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, in press.

(2) F. Sondheimer, R. Wolovsky and Y. Gaoni, *ibid.*, **82**, 754 (1960).

(3) *Inter al.*, see G. Eglinton and A. R. Galbraith, *J. Chem. Soc.*, **889** (1959); F. Sondheimer, Y. Amiel and R. Wolovsky, *J. Am. Chem. Soc.*, **81**, 4600 (1959).

(4) Sample placed on block just below this temperature.