

other ring maintains the highly stable cyclopentadienyl metal bond, thus enabling nickel to attain rare gas electron structure. The formation of  $C_{10}H_{10}Ni$  (dicyclopentadienylnickel) together with the  $C_{10}H_{12}Ni$  complex in the nickel carbonyl-cyclopentadiene reaction system<sup>1</sup> reveals the existence of hydrogen abstraction, which coupled with a transfer would clearly produce structure II.

Supporting evidence for structure II has been obtained through a study of the n.m.r. spectrum of the  $C_{10}H_{12}Ni$  complex coupled with an alternative synthesis. The strongest signal in the spectrum consists of a singlet with a chemical shift of  $-5.22$  p.p.m. relative to tetramethylsilane. This corresponds exactly to the shift displayed by the protons of a cyclopentadienyl group bonded to nickel and has been observed in our laboratory with other similarly bonded complexes.<sup>3</sup> The remaining portion of the spectrum consists of complex unresolved multiplets at  $-4.07$  p.p.m. and between  $-1.49$  to  $-0.76$  p.p.m. which have been assigned to protons on the 3-cyclopentenyl anion bonded to nickel. Because of the complexity of this part of the spectrum a correlation of protons and signals could not be made. Additional evidence for II was obtained by an alternative synthesis of the  $C_{10}H_{12}Ni$  complex involving reaction of the cyclopentadienyl and 3-cyclopentenyl anions with nickel bromide. Thus, to a dispersion of 11.0 g. (0.05 mole) of anhydrous nickel bromide in tetrahydrofuran maintained at  $-10^\circ$ , a solution of cyclopentadienylsodium (0.05 mole) in tetrahydrofuran was added over a period of one hour with rapid stirring under a protective atmosphere of pure nitrogen. This was followed by a tetrahydrofuran solution of 3-cyclopentenylmagnesium chloride (0.05 mole) also added over a period of one hour. The reaction mixture was maintained at room temperature for a period of 15 hours and all solvent then was removed at reduced pressures and room temperature. Sublimation of the residues at  $10^{-5}$  mm. and  $40^\circ$  yielded 1.0 g. of a reddish sublimate which was purified by fractional recrystallization from petroleum ether at temperatures of  $-10^\circ$ . In addition to some dicyclopentadienylnickel, 0.5 g. of a dark red, crystalline solid, m.p.  $43^\circ$  was isolated. Calcd. for  $C_{10}H_{12}Ni$ : C, 62.9; H, 6.35; Ni, 30.75. Found: C, 62.9; H, 6.15, Ni, 30.6. This crystalline solid was analytically identical with the monomeric and diamagnetic  $C_{10}H_{12}Ni$  complex, m.p.  $43^\circ$ , obtained by the reduction of dicyclopentadienylnickel with sodium amalgam in ethanol.<sup>2</sup> The infrared spectra of both materials were superimposable and correspond to the  $C_{10}H_{12}Ni$  complex, m.p.  $42^\circ$  reported by Fischer.<sup>1</sup>

(8) M. Dubeck, *J. Am. Chem. Soc.*, **82**, 6193 (1960).

We believe that the experimental results are good evidence in support of the cyclopentadienyl-3-cyclopentenylnickel(II) structure for the  $C_{10}H_{12}Ni$  complex, and suggest that the structural assignment by Fischer is in error. The recently reported 1,3-cyclohexadienecyclopentadienepalladium(0) complex<sup>4</sup> is also under investigation in our laboratory to determine whether the material could better be represented as 3-cyclohexenylcyclopentadienylpalladium(II) in analogy with the discussed nickel complex.<sup>5</sup>

(4) E. O. Fischer and H. Werner, *Ber.*, **93**, 2075 (1960).

(5) NOTE ADDED IN PROOF.—The possibility of structure II was first reported at the 138th Meeting of the American Chemical Society.<sup>2</sup> Since the submission of the present manuscript some n.m.r. data have been reported in support of II (E. O. Fischer and H. Werner, *Tetrahedron Letters*, **1**, 17 (1961)) and the general existence of transition metal bonded cyclic "en-yl" structures, an example of which we have reported previously.<sup>3</sup>

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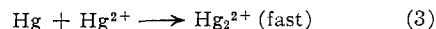
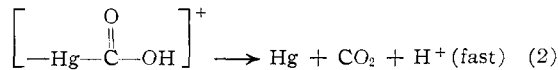
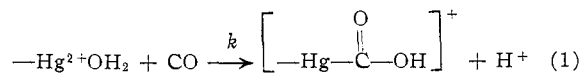
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### OXIDATION OF CARBON MONOXIDE BY METAL IONS

Sir:

Recent observations<sup>1</sup> that molecular hydrogen, although unreactive toward the majority of common inorganic oxidizing agents, is oxidized under relatively mild conditions in aqueous solution by a few metal ions and complexes, notably  $Cu^{2+}$ ,  $Ag^+$ ,  $Hg^{2+}$ ,  $Hg_2^{2+}$  and  $MnO_4^-$ , have prompted similar studies on another relatively inert reducing molecule, CO.

At temperatures below  $80^\circ$  only  $Hg^{2+}$  and  $MnO_4^-$ , among the ions listed above, showed measurable reactivity toward CO in aqueous solution;  $Fe^{3+}$ ,  $Tl^{3+}$  and  $Cr_2O_7^{2-}$  also were inactive. For the reduction of  $Hg^{2+}$ , *i.e.*,  $2Hg^{2+} + CO + H_2O \rightarrow Hg_2^{2+} + CO_2 + 2H^+$ , kinetic measurements in dilute  $HClO_4$  solution over the temperature range 26 to  $54^\circ$  yielded the rate law  $-d[CO]/dt = k[CO][Hg^{2+}]$  with  $\Delta H^* = 14.6$  kcal./mole and  $\Delta S^* = -13$  e.u. It is believed that the reaction proceeds by the mechanism (1), (2), (3), in which the first step involves insertion of CO between  $Hg^{2+}$  and a coordinated water molecule,



Support for this mechanism is provided by the observation<sup>2,3</sup> that when methanolic solutions of mercuric acetate take up CO under similar conditions, a stable methyl formate derivative,  $AcO-Hg-CO-OCH_3$ , analogous to the proposed intermediate, is formed and may be isolated.

The reduction of  $MnO_4^-$  by CO (to  $MnO_2$  in acid and neutral solutions and to  $MnO_4^{2-}$  in basic

(1) J. Halpern, *J. Phys. Chem.*, **63**, 398 (1959); *Advances in Catalysis*, **11**, 301 (1959).

(2) W. Schoeller, W. Schrauth and W. Essens, *Ber.*, **46**, 2864 (1913).

(3) J. Halpern and S. F. A. Kettle, *in press*.

solutions) was found to proceed readily over the temperature range 28 to 50°, and the earlier kinetic measurements on this system by Just and Kauko<sup>4</sup> 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  $\text{Ag}^+$  and  $\text{Hg}^{2+}$  (but not  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cd}^{2+}$  or  $\text{Tl}^{3+}$ ). 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  $\text{Hg}^{2+}$ . For  $\text{Ag}^+$ ,  $k(0^\circ) = 1.10 \times 10^5 M^{-2}\text{sec}^{-1}$ ,  $\Delta H^* = 1.2$  kcal./mole and  $\Delta S^* = -31$  e.u.; for  $\text{Hg}^{2+}$ ,  $k(0^\circ) = 1.06 \times 10^3 M^{-2}\text{sec}^{-1}$ ,  $\Delta H^* = 6.4$  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  $\text{Hg}^{2+}$ . It also seems likely that there exists a connection between the  $\text{Ag}^+$ -catalyzed oxidation of CO by  $\text{MnO}_4^-$  in solution and the very efficient oxidation of CO by solid  $\text{AgMnO}_4$ .<sup>5</sup>

Support of this work by the Alfred P. Sloan Foundation and the National Research Council of Canada is gratefully acknowledged.

(4) G. Just and Y. Kauko, *Z. physik. Chem.*, **82**, 71 (1913).

(5) M. Katz, *Advances in Catalysis*, **5**, 177 (1953).

(6) Alfred P. Sloan Research Fellow.

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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.<sup>1</sup> 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  $[\text{IrHCl}_2(\text{PPh}_3)_3]$ <sup>1</sup> 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	$\nu_{\text{IrH}}$ (cm. <sup>-1</sup> )
(I) $[\text{IrH}_3(\text{PPh}_3)_3]$	227–229°	Colorless	2100, 1745 <sup>b</sup>
(II) $[\text{IrH}_2\text{Cl}(\text{PPh}_3)_3]$	218–220	Colorless	2210, 2130 <sup>c</sup>
(III) $[\text{IrHCl}_2(\text{PPh}_3)_3]$ <sup>a</sup>	261–263	Pale yellow	2230 <sup>c</sup>

<sup>a</sup> Crystallizes with a molecule of benzene. <sup>b</sup> Chloroform solution. <sup>c</sup> Halocarbon mull.

$\text{AlD}_4$ ) shows absorption due to  $\nu_{\text{IrD}}$  at 1535 and 1255 cm.<sup>-1</sup>. 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 compounds<sup>1</sup> and (III) is similar in type to the recently reported hydrido complexes of rhodium and iridium.<sup>2</sup>

The author wishes to thank Dr. L. Vaska for the measurement of magnetic susceptibility, for supplying the first samples of the starting material and for useful discussion.

(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  $\pi$ -electron systems, were expected to be non-aromatic since they do not comply with Hückel's rule for aromaticity [presence of  $(4n + 2)$   $\pi$ -electrons].

1,5,9-Decatriyne<sup>2</sup> on oxidation with cupric acetate in pyridine<sup>3</sup> at 55° for 4 hr. yielded (besides other products)<sup>2</sup> 6% of the colorless cyclic dimer, 1,3,7,11,13,17-cycloeicosahexayne (I) [m.p. 230–231° dec.<sup>4</sup>;  $\lambda_{\text{max}}^{\text{isooctane}}$  226, 238 and 255  $\mu$ ; 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.