aldehyde function (2840, 2760, 1700 cm^{-1}) and the vinyl group (3090, 3010, 1635, 970, 905 cm^{-1}). The 100-MHz nmr spectrum (CCl_4–TMS) shows the following signals: δ 9.37, 1 H, four-line pattern with outer line spacing of 4.5 Hz and inner line spacing of 1.8 Hz ($HC{=}O$);[6] δ 5.9–5.5, 1 H, complex multiplet ($HC{=}C$); δ 5.24–4.94, 2 H, two overlapping sets of doublets of doublets, corresponding to the AB portion of an ABX pattern ($H_2C{=}C$); δ 2.20–1.95, 2 H, and 1.60–1.15, 2 H, complex multiplets assigned to the cyclopropane ring protons.

The behavior of I on glpc analysis offered the first clue to the tautomeric phenomenon. Invariably, under a variety of conditions (column material, temperature, and flow rate) the glpc trace of repeatedly purified I showed the presence of another component which peaked a short time before I and which tailed into the peak of I. Isolation of II in a state of >95% purity was accomplished in the following way: a sample of I, previously enriched in the more volatile component by slow distillation through a spinning-band column at reduced pressure, was injected into a preparative glpc column (10% Carbowax 1500 on Gas-Chrom P) held at 50° and the leading component was trapped. Recycling of the trapped fraction afforded II in increasing purity. The spectral properties of II contrast strongly with those of I and serve to establish its identity as 2,5-dihydrooxepin. The infrared spectrum of II reveals an intense band at 1655 cm^{-1}, characteristic of a vinyl ether, as well as the disappearance of the aldehydic absorptions noted for I. Strong bands at 1270 and 1105 cm^{-1}, attributable to C–O stretching modes, also appear. In the 100-MHz nmr spectrum (CCl_4–TMS), the aldehydic and vinyl signals of I have disappeared and new signals consistent with the dihydrooxepin structure have appeared: δ 6.13, 1 H, doublet of triplets with J values of 7.1, 1.7, and 1.7 Hz ($OC^7H{=}C$); δ 6.05–5.80, 2 H, complex multiplet ($C^3H{=}C^4H$); δ 4.50–4.15, 3 H, complex multiplets ($-C^2H_2-O$ and $HC^6{=}C$); δ 3.00–2.70, 2 H, complex multiplet ($-C^5H_2-$).[7]

At room temperature, II slowly reverts to I with a half-life of about 1 day to form an equilibrium mixture of 95% I and 5% II. Preliminary rate studies in the temperature range of 50–70° yield tentative values of $\Delta H^{\ddagger} = 23$ kcal/mol and $\Delta S^{\ddagger} = -6$ eu for the rearrangement of II to I.

The demonstration of the facile interconversion of I and II adds another example of concerted, bisallylic rearrangements of simple *cis*-disubstituted cyclopropanes to those already recorded.[8] In the present case, however, the cyclopropane derivative is favored at equilibrium, a result which reflects the balance of power when the driving force of carbonyl group formation is pitted against that of relief of cyclopropane ring strain.

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[6] The origin of this peculiar splitting pattern is being investigated. The complexity of the pattern has been found to be solvent, concentration, and temperature dependent. It may further be noted that the corresponding signal in *trans*-2-vinylcyclopropanecarboxaldehyde is a clean doublet with $J = 4.2$ Hz.

[7] These signals and their assignments find close correspondence with those reported for 2-oxabicyclo[3.2.1]octa-3,6-diene in ref 1.

[8] *cis*-Divinylcyclopropane → 1,4-cycloheptadiene (E. Vogel, R. H. Ott, and K. Gajek, *Ann.*, **644**, 172 (1961); W. von E. Doering and W. R. Roth, *Tetrahedron*, **19**, 715 (1963)); *cis*-2-vinylcyclopropyl isocyanate → 3,6-dihydro-2H-azepin-2-one (ref 4); Schiff bases of 1,2-diaminocyclopropane → 2,3-dihydro-1,4-diazepins (H. A. Staab and F. Vogtle, *Chem. Ber.*, **98**, 2701 (1965)).

[9] American Chemical Society Petroleum Research Fund Fellow, 1967–1968.

Preparation and Catalytic Properties of Some Cationic Iridium(III) and Rhodium(III) Dihydrido Complexes[1]

Sir:

Cleavage of the dimeric d^8 complexes, $[M(diene)Cl]_2$ (M = Ir, Rh),[2] with triphenylphosphine has previously led to the isolation of the neutral species, $M(diene)(PPh_3)Cl$.[3] We find that if the reaction is carried out in polar media such as alcohols or nitromethane, the cationic species, $[M(diene)(PPh_3)_2]^+$, are formed and can be isolated as tetraphenylborate or perchlorate salts.[4] We have prepared a series of these complexes with other ligands[5] as well as triphenylphosphine and find that the cationic iridum species are more readily formed and isolated than the corresponding rhodium complexes.

These d^8 complexes undergo a variety of oxidative addition and diene displacement reactions which will be described elsewhere.[6] This communication is concerned only with the interaction of these complexes with molecular hydrogen and the catalytic and related properties of the resultant dihydrido complexes.

The deep red acetone solution of the iridium cation, $[Ir(COD)(PPh_3)_2]^+$, undergoes immediate decolorization when treated with molecular hydrogen, and from the resultant solution, crystals of the cationic complex, $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$, can be isolated in good yield. The infrared spectrum (Nujol mull) of this complex shows, in addition to triphenylphosphine and uncoordinated anion modes, two bands at 2230 and 2260 cm^{-1} (metal–hydride stretching frequencies) and a strong, sharp doublet at 1650 and 1660 cm^{-1}, which we assign to coordinated acetone.[7] The infrared spectrum in chloroform shows the presence of both free (ν_{CO} ~1710 cm^{-1}) and coordinated (ν_{CO} ~1660 cm^{-1}) acetone, and, on addition of excess triphenylphosphine, the band at 1660 cm^{-1} disappears while the band at 1710 cm^{-1} increases in intensity. Moreover, on concentration of this solution the known cation,

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[1] Work supported by the William F. Milton Fund.

[2] diene refers to 1,5-cyclooctadiene (COD), norbornadiene (NBD), and 1,5-hexadiene.

[3] (a) G. Winkhaus and H. Singer, *Chem. Ber.*, **99**, 3610 (1966); (b) J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).

[4] Ionic species such as $[Ir(COD)(PPh_3)_2]^+$ were detected by conductivity measurements following an nmr study of these reactions: H. C. Volger, K. Vrieze, and A. P. Praat, *J. Organometal. Chem.*, **14**, 429 (1968); see also footnote, p 433. Ionic species in the rhodium system have previously not been observed.

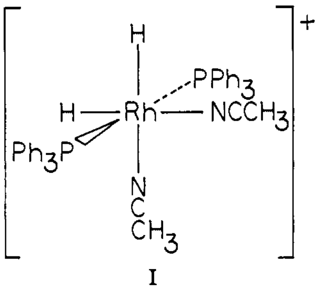
[5] J. A. Labinger and J. A. Osborn, to be submitted for publication.

[6] For example, interaction of these cations with carbon monoxide yields the five-coordinate cations $[M(PPh_3)_3(CO)_2]^+$, $[M(PPh_3)_2(CO)_3]^+$, as well as the solvated carbonyl species, $[Rh_2(PPh_3)_2(CO)_2(S)]^+$.

[7] The shift of ν_{CO} to lower frequency ($\Delta\nu_{CO} \sim 50$ cm^{-1}) indicates bonding of the keto group *via* oxygen. In the BF_3–acetone adduct, $\Delta\nu_{CO} \sim 60$ cm^{-1}; see B. F. Susz and P. Chalandan, *Helv. Chim. Acta.*, **41**, 1332 (1958). This can be contrasted with the bonding and spectral changes when perfluoroacetone coordinates to Pt(II); see B. Clarke, M. Green, R. B. L. Osborn, and F. G. A. Stone, *J. Chem. Soc.*, *A*, 167 (1968).

$[IrH_2(PPh_3)_4]^+$,[8] can be isolated. The nmr spectrum of the diacetone complex (0.1 *M* in $CDCl_3$) shows only one methyl resonance (relative intensity = 12) at τ 8.23 (at 28°). On addition of dry acetone, only one broad methyl resonance is observed, which is now shifted toward the free acetone resonance (at τ 7.91). Thus rapid exchange of free and coordinated acetone is occurring on the complex. Similar results are found for the analogous rhodium species.

Complexes with coordinated solvents such as acetonitrile, 2-butanone, dimethylacetamide, and ethyl alcohol are also readily isolated. Interestingly, however, the nmr spectrum of the bisacetonitrile–rhodium complex, $[RhH_2(PPh_3)_2(CH_3CN)_2]^+$, in dichloromethane at 28° shows a single sharp methyl resonance at τ 8.4, and, on addition of acetonitrile, two somewhat broad lines are observed at τ 8.1 and 8.4. In this case, the ligand exchange is considerably slower than in the diacetone complex.[9] The high-field overlapping triplets are at τ 27.4 ($J_{Rh-H} = 17.0$ Hz; $J_{P-H} = 13.0$ Hz). Taken with infrared evidence which indicates *cis*-hydrides and *cis*-acetonitriles, structure I is proposed for this complex.



I

These complexes function as homogeneous hydrogenation catalysts under mild conditions, *e.g.*, 5 m*M* acetone solutions of the iridium(III) cation, $[IrH_2(PPh_3)_2[(CH_3)_2CO]_2]^+$, catalytically hydrogenate 1,5-cyclooctadiene (0.5 *M*) at an initial rate of *ca.* 0.1 M^{-1} hr^{-1} at 25°.[10] Stepwise reduction occurs, cyclooctene being the initial product,[11] which is then more slowly converted into the saturated hydrocarbon. Interestingly, slow hydrogenation of butyraldehyde to give 1-butanol at 50° has been observed when this catalyst is used in dioxane solution.[12]

The analogous rhodium(III) cations, $[RhH_2(PPh_3)_2S_2]^+$ (S = solvent), can be prepared by treating a solution of the rhodium(I) species, $[Rh(NBD)(PPh_3)_2]^+$, with hydrogen in the requisite solvent. The complexes (S = $(CH_3)_2CO$, C_2H_5OH) dissolved in solvents such as tetrahydrofuran[13] very effectively catalyze the hydrogenation of olefinic and acetylenic bonds. Details of the catalytic process are still under study, but the following general observations may be noted at present.

(a) The rate of hydrogenation of monoolefins decreases in the sequence: hex-1-ene > cyclohexene ~ *cis*-hex-2-ene > *trans*-hex-2-ene ≫ 1-methylcyclohexene.

(b) Norbornadiene is reduced very rapidly, whereas 1,5- and 1,3-cyclooctadiene are reduced more slowly. Again, as in the iridium catalysis, intermediate formation of monoolefin is observed.

(c) Acetylenes are hydrogenated faster than the corresponding olefins: hex-1-yne > hex-2-yne > hex-1-ene.

(d) Unsaturated ketones and esters are readily hydrogenated without reduction of the carbonyl group.[14] The behavior with unsaturated aldehydes will be discussed elsewhere.

(e) The hydrogenation process is inhibited by the presence of excess triphenylphosphine or use of good donor solvents such as acetonitrile.

These general observations must be treated, however, with caution. We find that not only the absolute value but also the relative order of the rate of substrate reduction is strongly solvent dependent. We are currently investigating the possibility of using this solvent behavior to facilitate selective reductions, *e.g.*, inhibiting the reduction of dienes and acetylenes at the monoolefin stage.

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(8) M. Angoletta, *Gazz. Chim. Ital.*, **92**, 811 (1962).

(9) Temperature-dependent nmr studies are now in progress in order to investigate the relationship, if any, between the rate of solvent exchange and the catalytic efficiency of a given complex. In addition, the low-temperature studies will aid the structural elucidation of these dihydrido complexes which because of exchange processes show only ill-defined broad lines at high field at room temperature.

(10) Other dienes such as norbornadiene and 1,5-hexadiene are hydrogenated at about the same rate.

(11) Small amounts of 1,3- and 1,4-cyclooctadiene are formed during hydrogenation, possibly indicating that hydride transfer to the olefin in this system is stepwise and not synchronous.[14] If the structure of the active dihydrido species is as in I, stepwise transfer is also the most probable mechanism.

(12) *Cf.* R. S. Coffey, *Chem. Commun.*, 923 (1967).

(13) Other solvents we have used are dioxane, 2-methoxyethanol, dimethylacetamide, and acetone.

(14) *Cf.* J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc., A*, 1711 (1966).

(15) National Science Foundation Fellow.

(16) National Institutes of Health Fellow.

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Electrochemical Preparation of Cyclopropanediol Derivatives

Sir:

We wish to report what we believe to be the first examples of an intramolecular pinacol reduction leading to isolable cyclopropanediol derivatives. Cyclopropanediols themselves have been postulated as intermediates in the abnormal Clemmensen reduction of 1,3-diketones,[1] and a considerable body of inferential evidence has accumulated supporting this viewpoint.[2,3] This led us to search for conditions under which reduction of 1,3-diketones might be stopped at the cyclopropanediol state. The marked lability of cyclopropanols toward acids and bases[4] placed rather stringent limitations on the types of reducing agents which could be employed for this purpose, and we therefore undertook a study of the electrochemical reduction of diketones in nominally aprotic media.

The compound chosen for initial study was 2-methyl-2-acetylcyclohexanone, **1**, whose Clemmensen reduction was reported to lead to the rearranged products **2** and **3** *via* the diol **4a**.[2] As a probe into the electro-

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(1) D. Staschewski, *Angew. Chem.*, 71, 726 (1959).

(2) E. Wenkert and E. Kariv, *Chem. Commun.*, 570 (1965).

(3) (a) N. J. Cusack and B. R. Davis, *Chem. Ind.* (London), 1426 (1964); (b) K. M. Baker and B. R. Davis, *ibid.*, 768 (1966); (c) N. J. Cusack and B. R. Davis, *J. Org. Chem.*, **30**, 2062 (1965).

(4) C. H. De Puy, *Accounts Chem. Res.*, **1**, 33 (1968).