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REACTIONS OF SOME OXIRANES WITH RHODIUM(I) AND IRIDIUM(I) SPECIES

ROBERT B. OSBORNE and JAMES A. IBERS
Department of Chemistry, Northwestern University, Evanston, Illinois 60201 (U.S.A.)

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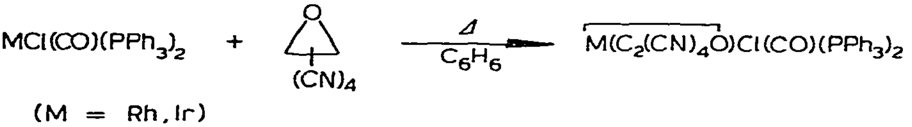
Summary

Tetracyanooxirane oxidatively adds to rhodium(I) and iridium(I) species to afford metal(III) compounds. With *trans*-$RhCl(CO)(PPh_3)_2$ a reaction in boiling C_6H_6 produces $RhCl(CN)(OC_2(CN)_3)(CO)(PPh_3)_2$, a rhodium(III)(cyano)(tricyanoenolato) compound. Characteristic frequencies are at 2225 (ν(C—C≡N)), 2106 (ν(Rh—C≡N)), 2009 (ν(C≡O)), and 1620 cm^{-1} (ν(C=C)). The nucleophilic *trans*-$IrCl(CO)(PMe_3)_2$ complex adds tetracyanooxirane at 25°C in THF to afford a stable oxametallacycle that shows a ν(C≡N) band at 2199 and a ν(C≡O) band at 2082 cm^{-1}. The unsaturated $MClP_2$ species (M = Rh, Ir; P = PPh_3) decarbonylate terminal oxiranes (phenyl- and vinyloxirane) to give *trans*-$MCl(CO)(PPh_3)_2$ compounds.

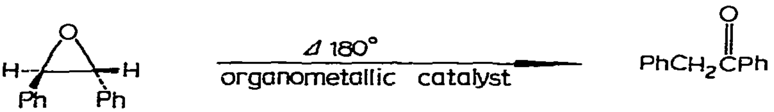
Introduction

The only reported additions of tetracyanooxirane to d^8 transition-metal centers are those by Lenarda et al., (eq. 1) [1].



(1)

However, these active d^8 metal centers are not inert towards other oxiranes. A kinetic study by Milstein et al. has uncovered isomerization of unactivated oxiranes by a number of d^8 metals, the best being rhodium(I) (eq. 2) [2,3]:



(2)

Most reactions of Rh and Pd species with oxiranes consist of ring-opening isomerization reactions to form ketones [3—5]. This paper is concerned with the reactions of varied rhodium(I) and iridium(I) species with several oxiranes.

Experimental

General procedures and starting materials. All reactions involving rhodium(I) and iridium(I) organometallic compounds were carried out under an atmosphere of pre-purified N_2. Fourier transform $^{31}P\{^1H\}$ NMR spectra were obtained with complete proton decoupling on a JEOL FX-90Q variable probe instrument. Infrared spectra were recorded on a Perkin—Elmer 283 IR spectrometer. All solvents used were distilled under N_2.

Tetracyanooxirane was prepared by a known method [6]. Phenyloxirane and *trans*-2,3-diphenyloxirane were purchased from Aldrich Chemical Co. The compound *trans*-2,3-dicyano-2,3-diphenyloxirane was prepared by a known method [7]. The following organometallic starting materials were prepared by published methods: $RhCl(CO)(PPh_3)_2$ [8], $(RhCl(PPh_3)_2)_2$ [9], $(RhCl(C_2H_4)_2)_2$ [10], $IrCl(CO)(PPh_3)_2$ [11], $IrCl(CO)(PMe_3)_2$ [12], and $(IrCl(C_8H_{14})_2)_2$ [13].

Elemental analyses were performed by H. Beck of Northwestern University and Micro-Tech Laboratories of Skokie, Ill.

Preparation of $RhCl(CN)(OC_2(CN)_3)(CO)(PPh_3)_2$

A reaction of 104.4 mg *trans*-$RhCl(CO)(PPh_3)_2$ (0.151 mmol) and 24.4 mg of tetracyanooxirane (0.169 mmol) was carried out in 15 ml of refluxing C_6H_6 for 10 min or more. Precipitation with hexane yielded 61% of a yellow solid. IR (Nujol): $\nu(C{\equiv}N)$ 2225, 2106, $\nu(C{\equiv}O)$ 2009, $\nu(C{=}C)$ 1620 cm^{-1}. $^{31}P\{^1H\}$NMR ($CDCl_3$): δ 42.5 (d, J (PRh) 24.4 Hz) downfield from phosphoric acid. M.p. 220°C (dec.). Anal. Found: C, 60.50; H, 3.83; N, 6.60. $C_{43}H_{30}ClN_4O_2P_2Rh$ calcd.: C, 61.85; H, 3.62; N, 6.71%.

When this reaction was carried out at room temperature, an orange product was obtained. The $\nu(C{\equiv}N)$ band at 2217 and the $\nu(C{\equiv}O)$ band at 2080 cm^{-1} indicated that the product was the oxametallocycle reported by Lenarda et al. [1].

Preparation of $\overline{Ir(C_2(CN)_4O})Cl(CO)(PMe_3)_2$

A reaction of 84.5 mg *trans*-$IrCl(CO)(PMe_3)_2$ (0.207 mmol) and 36.0 mg tetracyanooxirane (0.25 mmol) was carried out in 30 ml of THF at 25°C for 24 h. Dissolution of the starting materials produced an immediate change to a dark red-orange solution. Precipitation with hexane gave a 78% yield of a red-orange product. IR (Nujol): $\nu(C{\equiv}N)$ 2199, $\nu(C{\equiv}O)$ 2082 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ —43.3 (s, minor isomer) —34.5 (s, major isomer); minor dec. to $OPMe_3$ (37.9). M.p. 189°C. Anal. Found: C, 27.85; H, 3.66; N, 8.89. $C_{13}H_{18}ClIrN_4O_2P_2$ calcd.: C, 28.29; H, 3.29; N, 10.15%.

Reaction of $(RhCl(C_2H_4)_2)_2$ with phenyloxirane

A reaction of 39.5 mg $(RhCl(C_2H_4)_2)_2$ (0.102 mmol) and 109.1 mg PPh_3 (0.416 mmol) was carried out in 2.0 ml of phenyloxirane. At first a red homogeneous solution of "$RhCl(PPh_3)_2$" was generated; after 15 min a yellow solid precipitated and an orange suspension formed. The solid was separated by filtration after about 18 h and washed with 10 ml hexane. The yellow product, obtained in a 44% yield (on Rh), was identified as *trans*-$RhCl(CO)(PPh_3)_2$ by its IR spectrum and comparison with an authentic sample [8].

Reaction of $IrCl(C_8H_{14})_2)_2$ *with phenyloxirane*

A reaction of 187.7 mg $(IrCl(C_8H_{14})_2)_2$ (0.210 mmol) and 226.2 mg PPh_3 (0.86 mmol) was carried out in 5.0 ml of phenyloxirane. After 1 day a yellow solid was precipitated from solution, and after 5 days the product was filtered and dried. This light yellow product was a 32% yield of *trans*-$IrCl(CO)(PPh_3)_2$, identified by its IR spectrum and comparison with an authentic sample [11].

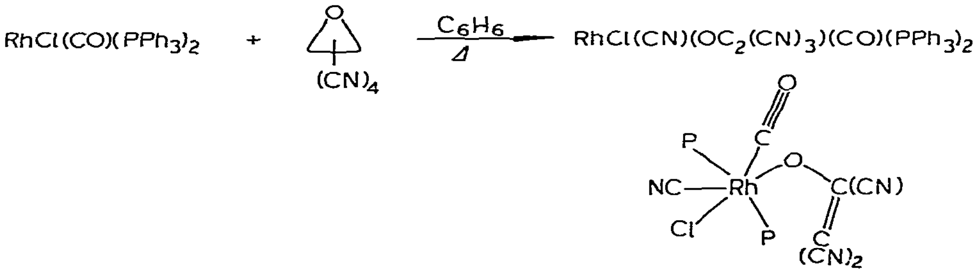
Other oxiranes

Reactions identical with those described above were carried out with an excess of vinyloxirane. This terminal oxirane was apparently opened to an aldehyde and decarbonylated by "$MClP_2$" in solution, but the final products were not clean as the organic residues formed polymers which were co-precipitated with the metal products. With *trans*-2,3-diphenyloxirane and *trans*-2,3-dicyano-2,3-diphenyloxirane there occurred some ring opening to ketones on reaction with "$IrClP_2$"; however, rhodium(I) species do not undergo this reaction at 25°C [3].

Results and discussion

Rh and Ir reactions

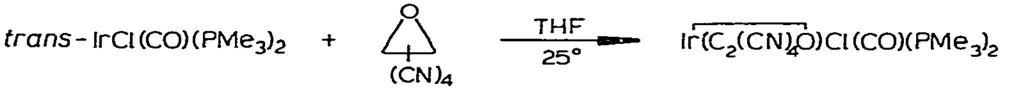
The oxidative addition of tetracyanooxirane to metal(I) centers at 80°C has been reported [1], but with $RhCl(CO)(PPh_3)_2$ the reaction must be carried out at room temperature in order to obtain a metallocycle. In refluxing C_6H_6 the following reaction occurs:



(3)

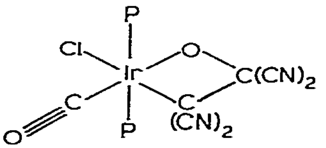
The product is not a metallacycle, but rather is the (cyano)(tricyanoenolato)-rhodium(III) compound, as deduced spectroscopically (ν(C—C≡N) 2225, ν(Rh—C≡N) 2106, ν(C≡O) 2009, and ν(C=C) 1620 cm^{-1}). This product is perhaps formed by a β-cyano-transfer reaction from the initially formed oxarhodiacycle [1]. The presumed structure of the metal(III) oxametallacycles is $\overline{M(C_2(CN)_4O})Cl(CO)(PPh_3)_2$, with the oxygen atom bonded in the α-position to the metal in the oxametallacycle, similar to the platinum(II) tetracyanooxametallacycles [14].

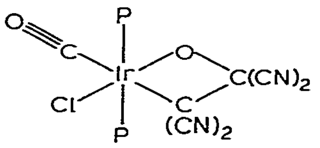
Since $IrCl(CO)(PPh_3)_2$ requires 80°C to add tetracyanooxirane, the more reactive PMe_3 analogue, $IrCl(CO)(PMe_3)_2$ [12], was synthesized. *Trans*-$IrCl(CO)(PMe_3)_2$ reacts rapidly with tetracyanooxirane at 25°C to afford by oxidative addition of red-orange oxairidiacyclobutane, $\overline{Ir(C_2(CN)_4O})Cl(CO)(PMe_3)_2$ (eq. 4).



(4)

The product was characterized by spectroscopic means. A broad infrared absorption at 2045—2100 cm^{-1} and centered at 2082 cm^{-1} is assigned to carbonyl absorption while a sharp band at 2199 cm^{-1} is assigned to a C—C≡N stretching mode [1]. The absence of P—P coupling in the $^{31}P\{^1H\}$ NMR spectrum is consistent with mutually trans phosphine groups. But since two singlets, one at —34.5 ppm and the other at —43.3 ppm, are observed we believe that the product is a mixture of the following two isomers:



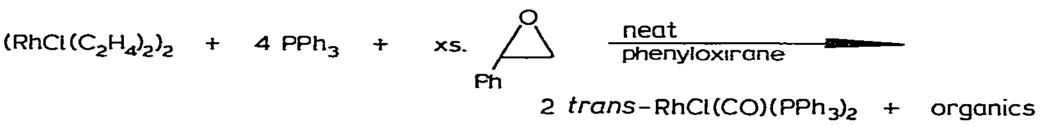


Presumably the carbonyl absorption is broadened because the C≡O stretching frequencies are slightly different in the two isomers. On the basis of the relative peak heights in the NMR spectrum, the distribution of isomers is approximately 7/3. The same reaction is observed at 0°C; the attack of the electron-rich iridium(I) center on the electrophilic oxirane is a facile process.

In sharp contrast the reactions of dicyanodiphenyloxiranes with this basic $IrCl(CO)(PMe_3)_2$ species did not afford readily identifiable products, although there were some indications of the formation of Ir^I cationic species [12].

Decarbonylation reactions

The 14-electron species "$MClL_2$" were generated by dissolving chloro-bridged dimers, such as $(RhCl(C_2H_4)_2)_2$ or $(IrCl(C_8H_{14})_2)_2$, in a suitable donor solvent and adding the required amount of tertiary ligand [15]. These "$MClL_2$" species decarbonylate a terminal oxirane:



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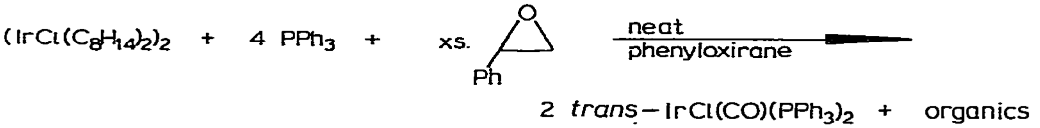

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The products, which are crystalline yellow compounds, are easily identified from their ν(C≡O) bands at 1983 cm^{-1} for Rh [8] and 1952 cm^{-1} for Ir [11].

Spectroscopic characterization of the organic by-products was unsuccessful owing to the presence of excess phenyloxirane. Although a similar reaction occurs with vinyloxirane, the metal products are apparently contaminated with organic polymers.

A reaction of the internal oxirane, *trans*-2,3-diphenyloxirane, with "IrCl-$(PPh_3)_2$" affords mainly benzylphenylketone and the $(IrClP_2)_2$ dimer. With rhodium(I) no isomerization occurs at 25°C. Similarly, with *trans*-2,3-dicyano-2,3-diphenyloxirane ring-opening occurs, at least to some extent, with iridium(I) but not with rhodium(I). As expected, the ketones formed in these reactions are inert to attack by the metal. The 14-electron "$MCl(PPh_3)_2$" [15] species (M = Rh, Ir) react rapidly with tetracyanooxirane, but amorphous brown solids were the only metal products recovered. On the basis of the IR spectra we believe the oxirane ring had opened.

Acknowledgments

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