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THE REACTIONS OF PLATINUM(0) AND PALLADIUM(0) TERTIARY PHOSPHINE COMPLEXES WITH PHENYL DICYANOOXIRANES

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Summary

The phenyldicyanooxiranes, *trans*-2,3-dicyano-2,3-diphenyloxirane, 2,2-dicyano-3,3-diphenyloxirane, and 2,2-dicyano-3-phenyloxirane, are cleaved by platinum(0) tertiary phosphine complexes to afford zerovalent metal—olefin complexes and phosphine oxides. The π-olefin products were characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy and by an X-ray structure determination of Pt[*trans*-Ph(CN)CC(CN)Ph]$(PPh_3)_2 \cdot CH_3OH$. Deoxygenation of the ring proceeds with retention of configuration in the final two-carbon olefin fragment. The π-complex $Pt[Ph_2CC(CN)_2](PPh_3)_2$ is isolable, but the olefin dissociates in the presence of alternative ligands. While $Pd[Ph(H)CC(CN)_2](PPh_3)_2$ may be isolated, the analogous complex with $Ph_2CC(CN)_2$ cannot be.

Introduction

Tri- and tetracyanooxiranes are known to yield oxametallocycles upon reaction with appropriate low-valent metal systems (eq. 1) [1,2]. For X = CN, M =

(1)

(M = Pt ; L = PPh_3, $P(p\text{-tol})_3$, $AsPh_3$ for $n = 4$, X = CN ;
L = PPh_3 for $n = 4$, X = H)

Pt, L = $AsPh_3$ the nature of the ring was established by diffraction methods and is shown in eq. 1 [2]. The proposed mechanism for this reaction is an S_N2 nucleophilic attack of the d^{10} platinum(0) center on an electropositive carbon atom of the ring, opening it to an ionic intermediate [2,3]. The intermediate

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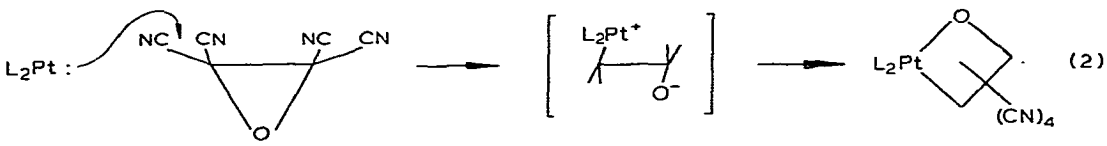
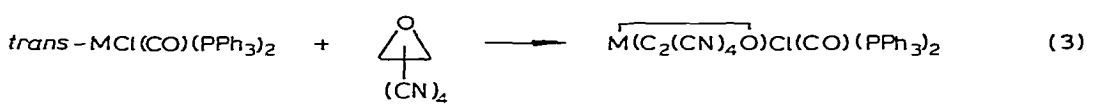
then undergoes a bond rotation about the C—C bond and closes to a metallacycle (eq. 2).



(2)

This postulate of nucleophilic attack was supported by the structure of the tricyanooxirane adduct, in which the lone hydrogen atom is attached to the β-carbon atom of the oxametallacycle [3]. The platinum atom thus selectively attacks the more electropositive dicyano carbon atom, which remains attached to the platinum center in the α-position [4]. These oxametallacycles may be isomerized to (cyano)(tricyanoenolato)platinum(II) compounds by heating, photolysis, or metathesizing with an alkyl phosphine [5].

Oxidative additions of tetracyanooxirane to d^8 rhodium(I) and iridium(I) compounds afford six-coordinate metal(III) oxametallacycles [6] (eq. 3). These

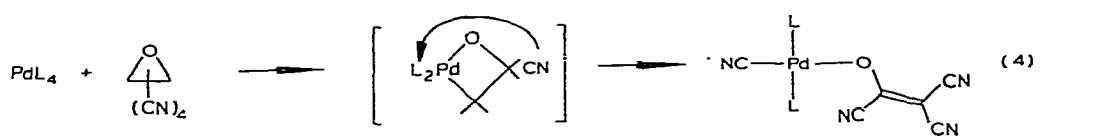


(3)

(M = Rh, Ir)

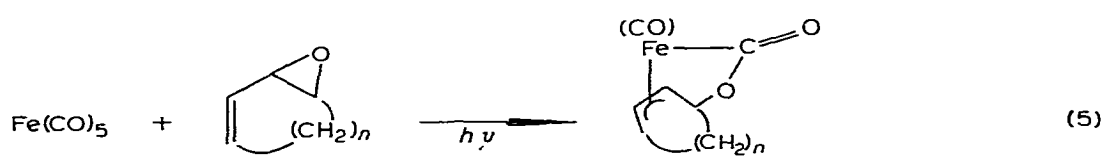
compounds have been characterized by IR spectroscopy, but the configuration of the ring was not specified.

With palladium(0) centers the reactions of tetracyanooxirane yield (cyano)-(tricyanoenolato)palladium(II) complexes (eq. 4). An intermediate oxametallacyclobutane has been postulated [6].



(4)

There is a brief report of a photochemical insertion of iron(0) into a vinyl oxirane to form (after a carbonyl insertion) an allyliron compound with a bridging carboxyl group (eq. 5) [7].



(5)

As an extension on the results with tri- and tetra-cyanooxirane we report here the reactions of phenyl-substituted dicyanooxiranes with platinum(0) and palladium(0) compounds. The products observed are metal—olefin complexes, with the attendant formation of phosphine oxides. The structure of one such platinum(0)—olefin complex, bis(triphenylphosphine)(*trans*-1,2-dicyano-1,2-diphenylethylene)platinum(0), is reported.

Experimental

General Procedures and Starting Materials

All reactions involving organometallic compounds were carried out under an atmosphere of pre-purified nitrogen, except where specifically noted. All solvents used were distilled under nitrogen. Fourier transform NMR spectra ($^{31}P\{^1H\}$ and ^1H) were obtained on a JEOL FX-90Q variable probe instrument and a Varian CFT-20 79.5 MHz spectrometer. Most of the $^{31}P\{^1H\}$ NMR spectra were recorded at −40°C, with samples under an atmosphere of N_2. Positive δ refers to a chemical shift downfield from phosphoric acid. Infrared spectra were recorded on a Perkin—Elmer 283 IR spectrometer.

The oxiranes used were prepared by methods previously described: *trans*-2,3-dicyano-2,3-diphenyloxirane by condensation of benzoyl cyanide and triethylphosphite with subsequent disproportionation [8] and the 2,2-dicyano oxiranes by epoxidation [9]. The olefins $Ph_2CC(CN)_2$ and $Ph(H)CC(CN)_2$ were obtained from the Aldrich Chemical Company.

All organometallic starting materials were prepared by published methods: $Pt(PPh_3)_4$ [10], $Pt(PEt_3)_4$ [11], $Pd(PPh_3)_4$ [12], and $Pd[P(p\text{-tolyl})_3]_3$ [13]. The ethyleneplatinum(0) complex may be prepared by the method described by Hartley [10], but a simpler method to obtain $Pt(C_2H_4)(PPh_3)_2 \cdot EtOH$ will be described below. The metal—dioxygen compounds $Pt(O_2)(PPh_3)_2$, $Pd(O_2)(PPh_3)_2$, and $Pd(O_2)[P(p\text{-tol})_3]_2$ were synthesized by bubbling O_2 through a C_6H_6 solution of PtP_4 or PdP_n [10]; the precipitates had ν(O—O) IR absorption bands of metal—peroxo compounds.

Elemental analyses were performed by H. Beck of Northwestern University, Micro-Tech Laboratories of Skokie, Illinois, and Galbraith Laboratories of Knoxville, Tennessee. All samples were checked for purity and identity by $^{31}P\{^1H\}$ NMR spectroscopy. This procedure does not detect the presence of non-phosphorus containing impurities. Since the samples could not be chromatographed and since in most instances they were obtained by hexane precipitation and were not recrystallized, the analyses, especially for %C, are often low.

Synthetic procedures

Preparation of $Pt(C_2H_4)(PPh_3)_2 \cdot EtOH$

A sample of 0.79 g *cis*-$PtCl_2(PPh_3)_2$ [10] (1.0 mmol) was weighed into a flask and the reaction system put under a flow of C_2H_4. The white solid was suspended in 10 ml absolute EtOH, and heated to 70°C with an oil bath. Next a 10% solution of $N_2H_4 \cdot H_2O$ (17.0 mmol) was dripped in slowly over a period of 20 min. The suspension first went to a homogeneous yellow solution, and then back to a suspension of a yellow solid. The ethylene flow was continued for an additional 2 h as the solution cooled, and then the yellow suspension was allowed to stir under a C_2H_4 atmosphere for 1 h. The yellow product was filtered and dried under vacuum; 0.52 g (0.65 mmol, 65% yield) of $Pt(C_2H_4)(PPh_3)_2 \cdot EtOH$ was isolated. The ^1H NMR spectrum of this complex showed EtOH with the expected spectrum of the ethylene complex. ^1H NMR ($CDCl_3$): δ 1.37 (t, CH_3, J 7.0 Hz); 1.53 (q, CH_2), 2.17 (C_2H_4, J(HPt) 60.4 Hz), 5.44 (s, OH). M.p. 120°C (dec.). Anal. Found: C, 60.54; H, 4.67; $C_{40}H_{40}OP_2Pt$ calcd.: C, 60.53; H, 5.07%.

Preparation of Pt[trans-Ph(CN)CC(CN)Ph](PPh$_3$)$_2$

A mixture of 453.9 mg Pt(C_2H_4)(PPh_3)$_2$ (0.608 mmol) and 303.5 mg *trans*-2,3-dicyano-2,3-diphenyloxirane (1.23 mmol) was allowed to react for 24 h in 20 ml THF. This reaction was terminated by precipitation with MeOH to obtain a 45% yield of the olefin complex. The complex was recrystallized from $CHCl_3$/MeOH for the X-ray study that provided the first indication of the nature of the reaction.

The same reaction was carried out with 82.1 mg Pt(C_2H_4)(PPh_3)$_2$·EtOH (0.104 mmol) and 34.0 mg of *trans*-2,3-dicyano-2,3-diphenyloxirane (0.138 mmol) in 20 ml toluene at 0°C for 4.5 h. Precipitation of the platinum product with hexane gave a 29% yield (on Pt) of product. The ^{31}P NMR spectrum revealed in addition to the platinum π-complex the presence of triphenylphosphine oxide. IR (Nujol mull): ν(C≡N) ~ 2201 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 30°C): δ 20.3 (s, J(PPt) 3640 Hz). M.p. 202°C (dec.). Anal. Found: C, 65.80; H, 4.39; N, 2.80; $C_{52}H_{40}N_2P_2Pt$ calcd.: C, 65.75; H, 4.24; N, 2.95%.

Preparation of Pt[Ph$_2$CC(CN)$_2$](PPh$_3$)$_2$

A. With 2,2-dicyano-3,3-diphenyloxirane: A mixture of 79.5 mg Pt(C_2H_4)(PPh_3)$_2$·EtOH (0.10 mmol) and 34.8 mg of 2,2-dicyano-3,3-diphenyloxirane (0.141 mmol) was stirred in 15 ml toluene for 18 h. A white solid precipitated from solution. Precipitation of more product with hexane and filtration netted a 72% yield of Pt($Ph_2CC(CN)_2$)(PPh_3)$_2$. A solution of the platinum—olefin compound must be stored in a dry box to maintain a π-olefin configuration; otherwise dissociation and oxidation take place. If Pt(PPh_3)$_4$ is used in place of Pt(C_2H_4)(PPh_3)$_2$, the product is a mixture of the platinum(0) π-complex and $OPPh_3$, with $OPPh_3$ in the residue as well (as detected by IR spectroscopy: 1193, 1121, and 721 cm^{-1}) [14].

B. With $Ph_2CC(CN)_2$: The same compound was prepared by direct reaction of 75.8 mg Pt(C_2H_4)(PPh_3)$_2$·EtOH (0.096 mmol) with 27.3 mg $Ph_2CC(CN)_2$ (0.12 mmol) in 10 ml toluene for 25 min at 0°C. Precipitation with hexane gave a 34% yield of the platinum(0)—olefin complex. IR (Nujol mull): ν(C≡N) 2208 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, —40°C) AX pattern, dd centered at δ 16.0 and 20.1 (J(PP) 14.0, J(PPt) 3070, 4360 Hz). M.p. 164°C (dec.). Anal. Found: C, 64.26; H, 3.96; N, 2.73; $C_{52}H_{40}N_2P_2Pt$ calcd.: C, 65.75; H, 4.24; N, 2.95%.

Preparation of Pt[Ph(H)CC(CN)$_2$](PPh$_3$)$_2$

A. With 2,2-dicyano-3-phenyloxirane: The reaction of 76.0 mg Pt(C_2H_4)(PPh_3)$_2$·EtOH (0.096 mmol) and 18.7 mg of 2,2-dicyano-3-phenyloxirane (0.10 mmol) in 15 ml toluene afforded a yellow solution. After 24 h the volume was reduced and Pt(Ph(H)CC(CN)$_2$)(PPh_3)$_2$ was precipitated with hexane in 47% yield. With Pt(PPh_3)$_4$ as a starting material a 1/1 mixture of Pt(Ph(H)CC(CN)$_2$)(PPh_3)$_2$ and $OPPh_3$ was obtained.

B. With Ph(H)CC(CN)$_2$: The metathesis of 75.6 mg Pt(C_2H_4)(PPh_3)$_2$·EtOH (0.095 mmol) and 18.9 mg Ph(H)CC(CN)$_2$ (0.12 mmol) in 15 ml toluene over 18 h gave a yellow solution. Precipitation with hexane produced a colorless solid in 72% yield. IR (Nujol mull): ν(C≡N) 2218, 2200 cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.45 (H, J(HPt) 50.9 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$, —40°C) AA′ pattern, s centered at δ 21.2 (J(PP) 22.0, J(PPt) 3260, 4360 Hz) (see Fig. 1).

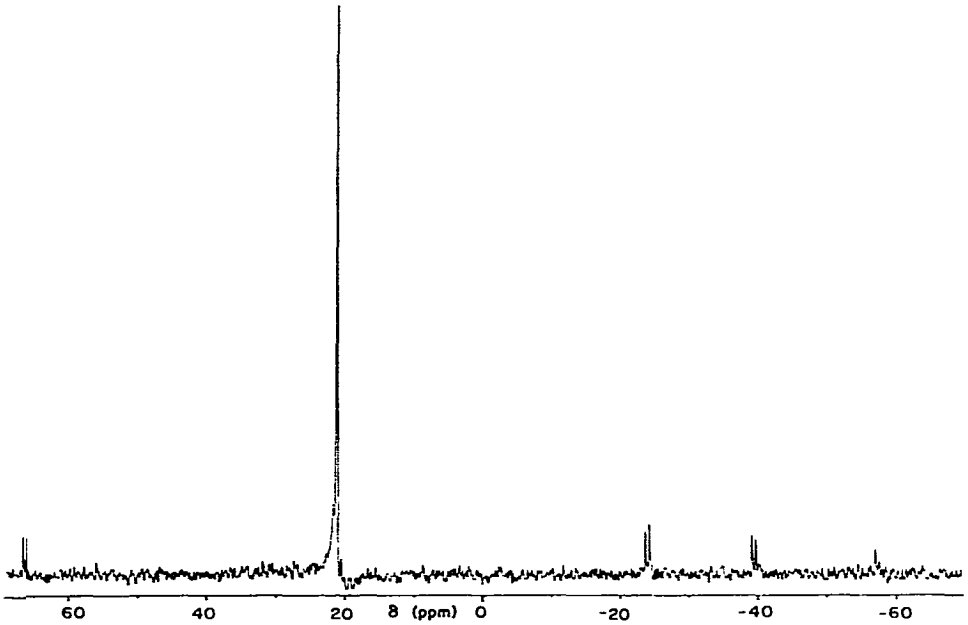


Fig. 1. $^{31}P\{^1H\}$ NMR Spectrum (36.2 MHz): $Pt[Ph(H)CC(CN)_2](PPh_3)_2$.

M.p. 186°C (dec.). Anal. Found: C, 62.74; H, 4.11; N, 3.05; $C_{46}H_{36}N_2P_2Pt$ calcd.: C, 63.23; H, 4.15; N, 3.21%.

Preparation of $Pt[Ph_2CC(CN)_2](PEt_3)_2$

A. With 2,2-dicyano-3,3-diphenyloxirane: The temperature-sensitive complex $Pt(PEt_3)_4$ (69.6 mg, 0.104 mmol) and 27.7 mg 2,2-dicyano-3,3-diphenyloxirane (0.113 mmol) were weighed out and stored at −40°C. Dissolution in 20 ml of toluene and warming to −20°C produced a pale yellow solution; after it was stirred for 24 h at 25°C the reaction mixture faded to a colorless solution. Precipitation with hexane gave a 22% yield of $Pt(Ph_2CC(CN)_2)(PEt_3)_2$. The residue contained $OPEt_3$.

B. With $Ph_2CC(CN)_2$: This same π-complex was synthesized by a metathesis reaction of 70.8 mg $Pt(PEt_3)_4$ (0.106 mmol) and 28.1 mg $Ph_2CC(CN)_2$ (0.12 mmol) on syringing in toluene at −30°C. A yellow solution was obtained on warming to 10°C; this was allowed to warm to 25°C and was stirred for 18 h. A white product was recovered in 54% yield. IR (Nujol mull): ν(C≡N) 2201 cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$, −40°C) AA′ pattern, s centered at δ 5.1 (J(PP) 14.0, J(PPt) 2890, 4060 Hz). M.p. 153°C (dec.). Anal. Found: C, 52.09; H, 5.84; N, 4.68; $C_{28}H_{40}N_2P_2Pt$ calcd.: C, 50.83; H, 6.09; N, 4.23%.

Preparation of $Pd[Ph(H)CC(CN)_2](PPh_3)_2$

A. With 2,2-dicyano-3-phenyloxirane: The reaction of 120 mg (0.104 mmol) of $Pd(PPh_3)_4$ and 49.0 mg of 2,2-dicyano-3-phenyloxirane (0.288 mmol) for 3.3 h in 20 ml THF at 0°C afforded a pale yellow solution. Precipitation with hexane gave a 61% yield of the yellow π-adduct $Pd(Ph(H)CC(CN)_2)(PPh_3)_2$.

B. With $Ph(H)CC(CN)_2$: A mixture of 120 mg $Pd(PPh_3)_4$ (0.104 mmol) and

48.8 mg $Ph(H)CC(CN)_2$ (0.316 mmol) in 20 ml of THF was stirred at 0°C for 3 h to give a light yellow solution. Precipitation with hexane gave a 49% yield (on Pd) of the product. Ir(Nujol mull): $\nu(C{\equiv}N)$ 2219, 2201 cm^{-1}. ^1H NMR

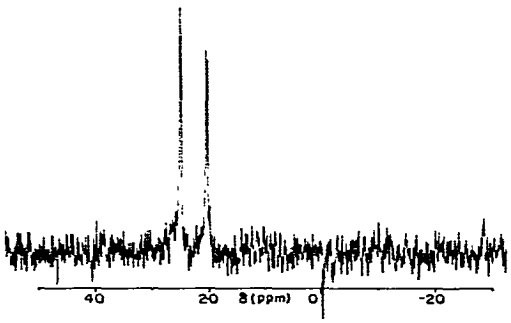


Fig. 2. $^{31}P\{^1H\}$ NMR Spectrum (36.2 MHz): $Pd[Ph(H)CC(CN)_2](PPh_3)_2$.

(C_6D_6): δ 5.35 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −30°C) AX pattern, dd centered at δ 20.3 and 24.9 (*J*(PP) 7.3 Hz) (See Fig. 2.). M.p. 143°C (dec.). Anal. Found: C, 67.45; H, 4.71; N, 3.50; $C_{46}H_{36}N_2P_2Pd$ calcd.: C, 70.37; H, 4.62; N, 3.57%.

Preparation of $Pd[Ph(H)CC(CN)_2](P(p\text{-}tol)_3)_2$

A. With 2,2-dicyano-3-phenyloxirane: A mixture of 102 mg $Pd[P(p\text{-tol})_3]_3$ (0.10 mmol) and 22.9 mg 2,2-dicyano-3-phenyloxirane (0.135 mmol) was stirred for 1.2 h in 20 ml THF at 0°C. Precipitation with hexane yielded 22% (on Pd) of the product.

B. With $Ph(H)CC(CN)_2$: When 76 mg $Pd[P(p\text{-tol})_3]_3$ (0.075 mmol) and 31.0 mg $Ph(H)CC(CN)_2$ (0.20 mmol) in 20 ml THF were stirred for 1.7 h at 0°C a yellow solution resulted. The volume was reduced and the residual solids washed with 5 ml hexane after decanting off the supernatant liquid. The π-complex was identified by its ^{31}P NMR spectrum. Recovery was only 18% on palladium. ^1H NMR (C_6D_6): δ 4.44 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, −40°C) AX pattern, dd centered at δ 18.3 and 23.1 (*J*(PP) 9.8 Hz). M.p. 158°C. Anal. Found: C, 71.15; H, 5.49; N, 5.32; $C_{62}H_{54}N_4P_2Pd$ calcd.: C, 72.76; H, 5.32; N, 5.47%.

Attempted reactions of PdP_n with 2,2-dicyano-3,3-diphenyloxirane

Reactions of $Pd(PPh_3)_4$ and $Pd[P(p\text{-tol})_3]_3$ with 2,2-dicyano-3,3-diphenyloxirane were attempted; a deoxygenation reaction apparently takes place, but the palladium(0) π-olefin complexes of $Ph_2CC(CN)_2$ were not isolable. In several reactions a palladium(II) dioxametallacycle was recovered from solution as a result of a reaction of the olefin with small amounts of adventitious dioxygen. This assignment was verified by the synthesis of authentic samples of these compounds. The general procedure follows the literature method [15] and details are given below for new compounds synthesized here.

Preparation of $\overline{Pd(C(CN)_2CPh_2OO)}(PPh_3)_2$

A reaction of $Pd(O_2)(PPh_3)_2$ (67.9 mg, 0.101 mmol) and 28.7 mg $Ph_2CC(CN)_2$

(0.125 mmol) was run for 3h at 0°C in 20 ml THF. Precipitation with hexane yielded 72% (on Pd) of the expected dioxapalladiacycle [15]. The ^{31}P NMR spectrum of this compound is an A—B doublet of doublets, a characteristic pattern observed for these palladium(II) complexes. $^{31}P\{^1H\}$ NMR ($CDCl_3$, —40°C) AB pattern, dd centered at δ 26.6 and 28.5 (*J*(PP) 34.2 Hz). M.p. 84°C (dec.). Anal. Found: C, 67.33; H, 4.52; N, 3.21; $C_{52}H_{40}N_2O_2P_2Pd$ calcd.: C, 69.92; H, 4.51; N, 3.14%.

Preparation of $Pd[C(CN)_2CPh_2OO][P(p\text{-}tol)_3]_2$

A mixture of 19 mg $Pd(O_2)(P(p\text{-}tol)_3)_2$ (0.026 mmol) and 15.9 mg $Ph_2CC(CN)_2$ (0.069 mmol) was stirred in 20 ml THF for 3 h at 0°C. This gave a yellow solution from which the dioxametallocycle was precipitated in 36% yield. $^{31}P\{^1H\}$ NMR ($CDCl_3$, —40°C) AB pattern, dd centered at δ 24.8 and 26.6 (*J*(PP) 34.2 Hz). M.p. 120—125°C (dec.). Anal. Found: 68.01; H, 5.52; N, 2.61; $C_{58}H_{52}N_2O_2P_2Pd$ calcd.: C, 71.27; H, 5.36; N, 2.87%.

Preparation of $Pd[C(CN)_2CPh(H)OO][P(p\text{-}tol)_3]_2$

A mixture of 19 mg $Pd(O_2)(P(p\text{-}tol)_3)_2$ (0.026 mmol) and 13.3 mg (0.086 mmol) of $Ph(H)CC(CN)_2$ in 20 ml THF was stirred for 3h at 0°C. Precipitation with hexane gave 70% (on Pd) of the desired light yellow product. ^1H NMR (C_6D_6): δ 5.35 (s). $^{31}P\{^1H\}$ NMR ($CDCl_3$, —40°) AB pattern, dd centered at δ 24.4 and 25.4 (*J*(PP) 33.6 Hz). M.p. 193°C (dec.). Although spectral data support the synthesis, satisfactory elemental analyses could not be obtained.

X-ray Analysis of $Pt[trans\text{-}Ph(CN)CC(CN)Ph](PPh_3)_2 \cdot CH_3OH$

The compound was recrystallized from hot $CHCl_3$/MeOH to give small, clear crystals. These crystals rapidly lose methanol of solvation. Data collection and solution of the structure proceeded by methods standard in this laboratory [16]. Some details are given in Table 1. In the final full-matrix, least-squares refinement the following model was used: (i) each phenyl group was treated as a rigid group of D_{6h} symmetry and the carbon atoms were assigned individual, variable isotropic thermal parameters; (ii) all other non-hydrogen atoms were refined anisotropically; (iii) hydrogen atoms were included in idealized positions as fixed contributions to the structure factors (C—H 0.95 Å, B(H) = B(C) + 0.5 Å^2); (iv) refinement was on F and involved 196 variables and 6412 observations. This refinement converged to final values of R and R_w of 0.045 and 0.053 and to an error in an observation of unit weight of 1.69 e. The main features on a final difference electron density map were two peaks of height 2.6(2) and 2.5(2) e/Å^3 on either side of the platinum atom. An analysis of $\Sigma w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, Miller indices, and setting angles revealed no unusual trends.

Positional parameters for the atoms are tabulated in Table 2. Tables 3 * and 4 * provide more complete parameter information while Table 5 * presents root-mean-square amplitudes of vibration. Table 6 * presents a listing of $10|F_o|$ vs. $10|F_c|$ for reflections used in the refinement.

TABLE 1

DATA COLLECTION PROCEDURES AND REFINEMENT RESULTS FOR Pt[*trans*-Ph(CN)CC(CN)Ph]·$(PPh_3)_2$·CH_3OH

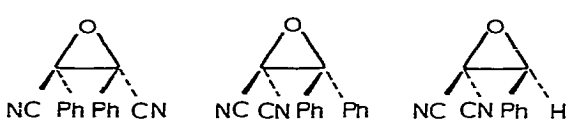
Formula	$C_{53}H_{44}N_2OP_2Pt$
Formula weight	981.99 amu
Space group	C_i^1—$P\bar{1}$
a	11.549(9) Å
b	20.93(1) Å
c	9.411(7) Å
α	93.70(3)°
β	108.28(2)°
γ	89.04(2)°
Z	2
Temperature	—150°C [a]
ρ_c	1.514 g/cm^3 (at —150°C)
ρ_o	1.43 g/cm^3 (at 25°C) [b]
Crystal shape	Needle of hexagonal cross section bounded by faces of the forms $\{100\}$, $\{110\}$ and $\{1\bar{1}0\}$.
Crystal volume	0.00585 mm^3
Radiation	graphite monochromated Mo-K_α; (λ(Mo-K_{α_1}) 0.7093 Å)
μ	34.0 cm^{-1}
Transmission factors	0.57 to 0.79
Take-off angle	3.4°
Receiving aperture	5.3 × 5.6 mm, 34 cm from the crystal
Scan speed	2°/min
Scan width	1.0° below K_{α_1} to 1.0° above K_{α_2}; above 2θ = 30.5°, 1.1° above K_{α_2}
Data collection	$\theta/2\theta$ method, $3.5° \leq 2\theta \leq 50.0°$; $\pm h, \pm k, l \geq 0$ collected
Background counts	10 seconds, with rescan option [c]
No. reflections measured	8138
Unique data with $F_o^2 > 3\sigma(F_o^2)$	6412
No. of variables	196
Error in observation	1.69 e
Final R (on $\|F_o\|$ for $F_o^2 > 3\sigma(F_o^2)$)	0.045
Final R_w (on $\|F_o\|$ for $F_o^2 > 3\sigma(F_o^2)$)	0.053

[a] The low temperature system is based on a design by Huffman [17]. [b] By $ZnCl_2$ flotation method. [c] The diffractometer was run under the disk-oriented Vanderbilt system [18].

Results

Reactions

The phenyldicyanooxiranes utilized in this study are:



(I) (II) (III)

When compounds I—III are allowed to react with $Pt(C_2H_4)(PPh_3)_2$·EtOH in THF or toluene solutions under an inert atmosphere deoxygenation of the

* Tables 3, 4, 5, and 6 have been deposited as NAPS document 03937 (25 pages). Order from NAPS c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017. Remit in advance, in U.S. funds only $9.25 for photocopies or $4.00 for microfiche. Outside the U.S. and Canada add postage of $5.50 for photocopy and $1.50 for microfiche.

TABLE 2

POSITIONAL PARAMETERS FOR Pt[*trans*-Ph(CN)CC(CN)Ph](PPh_3)$_2$·CH_3OH

ATOM	X	Y	Z
PT	0.218586(28)	0.251062(15)	0.197469(34)
P(1)	0.33005(17)	0.158316(88)	0.23472(22)
P(2)	0.36416(17)	0.329275(89)	0.24163(22)
C(1)	0.04387(66)	0.29071(34)	0.11112(84)
C(2)	0.03474(67)	0.22036(34)	0.12887(84)
C(3)	0.00207(66)	0.33367(34)	0.21415(85)
C(4)	0.00293(66)	0.18386(34)	-0.01397(86)
N(1)	-0.03098(60)	0.36913(31)	0.28953(76)
N(2)	-0.02476(61)	0.15473(31)	-0.12975(78)
O(1)	-0.23865(55)	0.44242(28)	0.35852(70)
C(5)	-0.18562(92)	0.43846(48)	0.4423(12)
C(11)	-0.06897(48)	0.35383(28)	-0.33810(45)
C(12)	-0.15219(35)	0.35158(28)	-0.25877(58)
C(13)	-0.11432(39)	0.33220(26)	-0.11256(56)
C(14)	0.00676(43)	0.31508(25)	-0.04568(44)
C(15)	0.08997(33)	0.31733(26)	-0.12500(56)
C(16)	0.05211(43)	0.33670(28)	-0.27121(55)
C(21)	-0.10205(51)	0.14219(26)	0.45605(53)
C(22)	-0.14327(46)	0.11820(23)	0.30730(59)
C(23)	-0.09864(48)	0.14348(24)	0.20141(43)
C(24)	-0.01277(46)	0.19275(23)	0.24427(49)
C(25)	0.02843(43)	0.21674(22)	0.39302(54)
C(26)	-0.01618(51)	0.19146(26)	0.49891(42)
C(31)	0.20833(44)	0.09009(20)	0.38460(45)
C(32)	0.13446(47)	0.04174(23)	0.40432(44)
C(33)	0.08923(44)	-0.00599(20)	0.29106(56)
C(34)	0.11787(47)	-0.00537(20)	0.15807(48)
C(35)	0.19174(47)	0.04298(23)	0.13834(43)
C(36)	0.23697(42)	0.09071(20)	0.25161(52)
C(41)	0.42456(54)	0.09905(30)	-0.19680(50)
C(42)	0.31190(47)	0.12546(29)	-0.20206(45)
C(43)	0.28707(37)	0.14346(26)	-0.06961(58)
C(44)	0.37483(46)	0.13501(25)	0.06810(46)
C(45)	0.48755(41)	0.10859(27)	0.07337(49)
C(46)	0.51238(41)	0.09060(29)	-0.05908(64)
C(51)	0.67241(38)	0.13028(22)	0.64176(48)
C(52)	0.62435(44)	0.19123(18)	0.61211(51)
C(53)	0.52131(44)	0.19950(16)	0.48923(55)
C(54)	0.46631(37)	0.14682(21)	0.39608(47)
C(55)	0.51436(43)	0.08587(18)	0.42564(51)
C(56)	0.61741(44)	0.07760(17)	0.54852(56)
C(61)	0.67874(39)	0.25557(26)	0.07361(57)
C(62)	0.70532(33)	0.27674(27)	0.22371(53)
C(63)	0.61271(43)	0.30859(25)	0.27757(40)
C(64)	0.49353(37)	0.30328(24)	0.18134(52)
C(65)	0.46695(34)	0.28211(25)	0.03125(48)
C(66)	0.55956(45)	0.25826(25)	-0.02261(42)
C(71)	0.49551(47)	0.41346(24)	0.72989(40)
C(72)	0.54980(40)	0.43389(21)	0.62783(52)
C(73)	0.51219(42)	0.40816(22)	0.48037(47)
C(74)	0.42027(43)	0.36201(22)	0.43498(40)
C(75)	0.36597(39)	0.34158(21)	0.53705(53)
C(76)	0.40359(46)	0.36731(24)	0.68450(48)
C(81)	0.21068(46)	0.51050(20)	-0.00659(58)
C(82)	0.16136(40)	0.48696(22)	0.09705(60)
C(83)	0.21168(43)	0.43309(22)	0.17274(52)
C(84)	0.31130(42)	0.40276(19)	0.14478(54)
C(85)	0.36062(40)	0.42630(22)	0.04115(58)
C(86)	0.31031(47)	0.48017(24)	-0.03454(55)
H1C(11)	-.0947	.3672	-.4380
H1C(12)	-.2348	.3633	-.3047
H1C(13)	-.1711	.3307	-.0587
H1C(15)	.1727	.3058	-.0795
H1C(16)	.1090	.3385	-.3255
H1C(21)	-.1325	.1248	.5287
H1C(22)	-.2019	.0844	.2785
H1C(23)	-.1271	.1270	.1001
H1C(25)	.0865	.2504	.4223
H1C(26)	.0117	.2078	.6006
H1C(31)	.2386	.1226	.4617
H1C(32)	.1144	.0412	.4949
H1C(33)	.0386	-.0391	.3044
H1C(34)	.0869	-.0381	.0807
H1C(35)	.2111	.0433	.0476
H1C(41)	.4417	.0869	-.2876
H1C(42)	.2521	.1313	-.2963
H1C(43)	.2103	.1613	-.0733
H1C(45)	.5476	.1026	.1670
H1C(46)	.5894	.0726	-.0559
H1C(51)	.7428	.1246	.7257
H1C(52)	.6619	.2271	.6759
H1C(53)	.4886	.2411	.4691
H1C(55)	.4769	.0499	.3620
H1C(56)	.6503	.0360	.5688
H1C(61)	.7419	.2394	.0362
H1C(62)	.7868	.2748	.2888
H1C(63)	.6310	.3148	.3798
H1C(65)	.3856	.2840	-.0347
H1C(66)	.5414	.2440	-.1256
H1C(71)	.5212	.4311	.8308
H1C(72)	.6124	.4655	.6590
H1C(73)	.5493	.4221	.4110
H1C(75)	.3037	.3099	.5066
H1C(76)	.3668	.3533	.7546
H1C(81)	.1761	.5472	-.0586
H1C(82)	.0928	.5075	.1155
H1C(83)	.1776	.4170	.2431
H1C(85)	.4288	.4058	.0225
H1C(86)	.3440	.4963	-.1050
H1C(5)	-.1059	.4894	.5112
H2C(5)	-.1750	.5301	.3786
H3C(5)	-.2346	.5160	.4999

oxirane ring occurs with formation of phosphine oxide and a platinum(0)—olefin compound:

$$Pt(C_2H_4)(PPh_3)_2 \cdot EtOH + I - III \xrightarrow[25°C]{\text{THF or toluene}} Pt(olefin)(PPh_3)_2 + OPPh_3 \quad (6)$$

The nature of the reaction (eq. 6) was first established through the determination of the structure of the platinum-containing product from oxirane I (vide infra). This structure established the product to be Pt [*trans*-Ph(CN)CC(CN)Ph]-$(PPh_3)_2 \cdot CH_3OH$, rather than the expected oxaplatinacyclobutane product. With this information available it was possible to identify the platinum products from ensuing reactions by their $^{31}P\{^1H\}$ NMR spectra and to identify phosphine oxides by characteristic bands in the IR region (1195, 1120, and 720 cm^{-1}) [14].

Test reactions were carried on the dicyanooxiranes by adding a 2/1 excess of free triphenylphosphine to solutions of I, II, and III and stirring for a number of hours. No significant oxidation of the phosphine by the oxirane was detected; starting materials were recovered essentially unchanged.

When the reaction (eq. 6) of I was quenched after a short reaction time at 0°C, the $^{31}P\{^1H\}$ NMR spectrum of the recovered product indicated approximately equimolar amounts of the olefin-platinum(0) complex and triphenylphosphine oxide. The yield for these reactions is about 40%, as the source of the phosphine for reduction is a species generated upon dissolution of the starting materials.

The nucleophilic mechanism of metal-mediated oxirane ring opening [2,3] requires an electropositive carbon atom for the initial metal attack. Oxiranes II and III were utilized since we anticipated that the metal would attack the dicyano carbon atom of the ring, while the oxide would be attached to the carbon atom with electropositive substituents. But again the products were metal—olefin complexes and phosphine oxides. Reactions of oxiranes II or III with $Pt(PPh_3)_4$ were carried out under similar conditions; the products were again a metal—olefin complex and triphenylphosphine oxide. The yields were enhanced to the degree that an excess of free phosphine in solution promoted the deoxygenation reaction. The reaction of $Pt(PPh_3)_4$ with I was not clean and gave a mixture of products.

The compound $Pt(PEt_3)_4$ was used in reaction 6 to probe the effect of a more basic phosphine on the metal-induced ring opening reaction. With II, the olefin $Pt[Ph_2CC(CN)_2](PEt_3)_2$ was isolated as a white solid. Similar reactions with I and III afford, on the other hand, intractable mixtures of platinum(II) products.

The related $Pd(PPh_3)_4$ and $Pd[P(p\text{-tol})_3]_3$ species are observed to deoxygenate oxirane III to form palladium(0) π-complexes. The optimal reaction conditions are 1 to 4 h at 0°C in dilute THF solution. If the reactions are carried out in less polar solvents or at 25°C, a complex mixture of palladium products is obtained. The palladium(0)—olefin products from III can be isolated; but the compounds must be stored under argon. The olefin complexes resulting from II, however, are not stable in solution although the deoxygenation reaction was established spectroscopically. No reaction of oxirane I with $Pd(PPh_3)_4$ was observed at 0°C; reactions run in refluxing THF afforded a mixture of products.

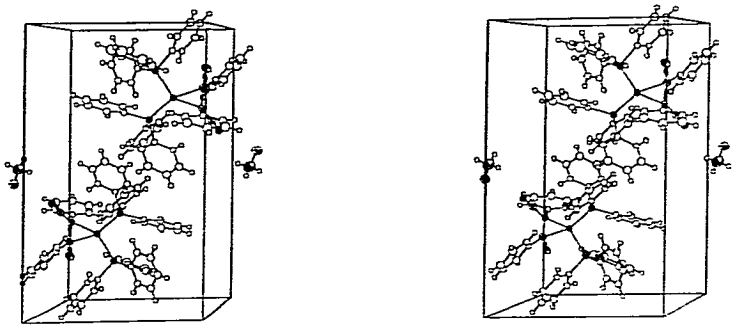


Fig. 3. A stereoview of the unit cell of Pt[*trans*-Ph(CN)CC(CN)Ph]$(PPh_3)_2 \cdot CH_3OH$. The view is down the c axis. The 60% probability ellipsoids are shown here and in subsequent figures.

TABLE 7

DISTANCES AND ANGLES FOR Pt[*trans*-Ph(CN)CC(CN)Ph]$(PPh_3)_2 \cdot CH_3OH$

Distances (Å)		Angles (°)	
Pt—P(1)	2.295(2)	P(1)—Pt—P(2)	103.51(9)
Pt—P(2)	2.289(2)	C(1)—Pt—C(2)	41.7(3)
Pt—C(1)	2.102(7)	P(1)—Pt—C(2)	104.6(2)
Pt—C(2)	2.113(8)	P(2)—Pt—C(1)	110.0(2)
C(1)—C(2)	1.50(1)	C(1)—C(2)—Pt	68.7(4)
C(1)—C(3)	1.47(1)	C(2)—C(1)—Pt	69.5(4)
C(2)—C(4)	1.45(1)	C(1)—C(3)—N(1)	176.8(8)
C(1)—C(14)	1.521(9)	C(2)—C(4)—N(2)	178.8(8)
C(2)—C(24)	1.51(1)	C(3)—C(1)—C(14)	111.5(6)
C(3)—N(1)	1.14(1)	C(4)—C(2)—C(24)	114.6(6)
C(4)—N(2)	1.17(1)	C(3)—C(1)—C(2)	115.9(7)
		C(4)—C(2)—C(1)	111.7(7)
P(1)—C(36) [a]	1.835(5)	C(14)—C(1)—C(2)	119.2(6)
P(1)—C(44)	1.835(6)	C(24)—C(2)—C(1)	124.3(7)
P(1)—C(54)	1.836(4)	C(5)—O(1)—N(1)	131.7(8)
P(2)—C(64)	1.820(6)	Pt—P—C(x4)	115(5)
P(2)—C(74)	1.821(4)	C(x4)—P—C(y4)	104(3)
P(2)—C(84)	1.835(5)	Phenyl groups: Conform to a D_{6h} point group, all angles 120° and all C—C distances set to 1.392 Å	
Avg. P—C	1.830(8)		
C(5)—O(1) [b]	1.40(1) [a]		

Dihedral angles	
C(3)C(1)C(14)—C(24)C(2)C(4)	64.1(8) (α) [c]
PtP(1)P(2)—PtC(1)C(2)	8.9(4) (θ)
Vector - plane normal angles	
C(1)C(2)—C(3)C(1)C(14)	55.2(8) (β_1)
C(1)C(2)—C(24)C(2)C(4)	60.8(9) (β_2)
C(1)C(2)—PtP(1)P(2)	83.2(4) (ψ)
Torsion angles	
C(3)C(1)C(2)C(4)	144.2(7) (γ_1)
C(14)C(1)C(2)C(24)	138.0(6) (γ_2)
PtC(2)C(1)C(3)	110.5(5) (δ_1)
PtC(1)C(2)C(4)	105.3(6) (δ_2)
PtC(2)C(1)C(14)	112.0(7) (δ_3)
PtC(1)C(2)C(24)	110.0(6) (δ_4)

[a] Atoms C(36) and C(x4) ($x > 3$) of phenyl ring x are attached to P atoms, and the atoms of a given ring are C(x1) through C(x6) ($x \geq 3$). [b] Atoms C(5) and O(1) belong to the methanol of solvation. [c] The angles α—δ, θ, ψ are defined in ref. 19.

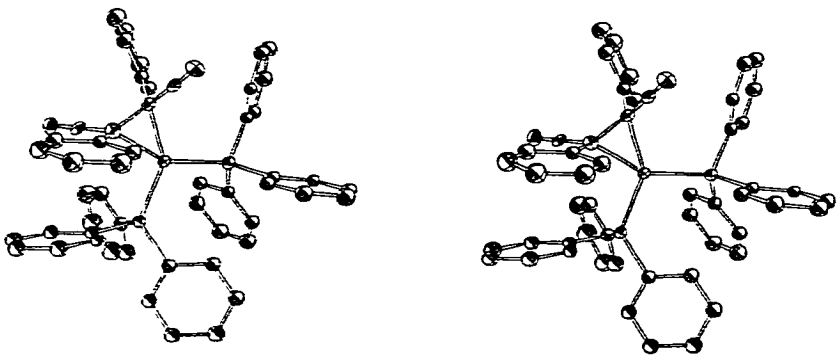


Fig. 4. A stereoview of the Pt[*trans*-Ph(CN)CC(CN)Ph](PPh$_3$)$_2$ molecule.

In the presence of adventitious dioxygen olefins II and III form dioxametallacycles [15] with these metal species.

Description of the structure of Pt (trans-(Ph(CN)CC(CN)(Ph)(PPH$_3$)$_2$ · CH$_3$OH

The unit cell (Fig. 3) contains two platinum-containing molecules and two methanol molecules. Table 7 presents metrical information on the platinum-olefin complex. The C(5)—O(1)—N(1) bond angle (131.7(8)°) and the O(1)—N(1) distance (3.04(1) Å) suggest that a weak hydrogen bond may be joining solvent to molecule.

The structure is the expected square-planar configuration for a d^{10} platinum(0) center, with the olefinic carbon—carbon double bond in the PtP$_2$ plane. A stereoview of the molecule is shown in Fig. 4 and a perspective draw-

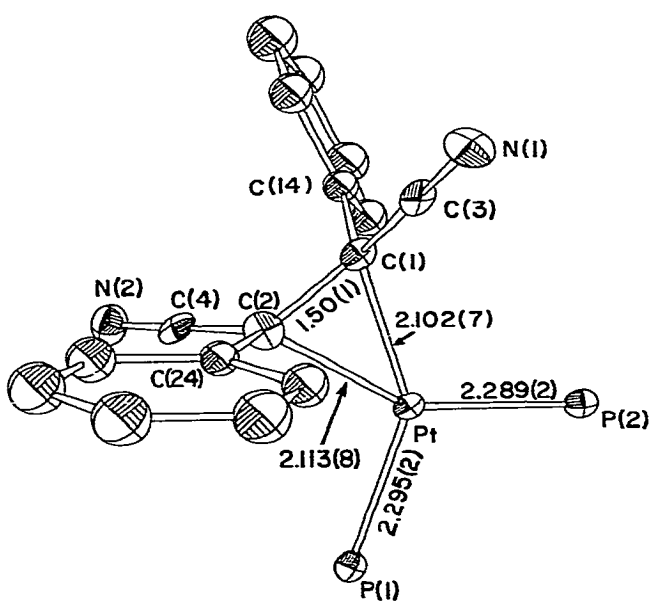
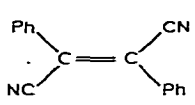
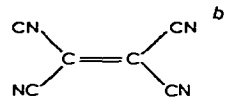
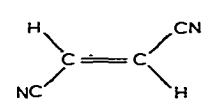
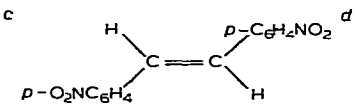


Fig. 5. A perspective drawing of the inner coordination sphere of Pt[*trans*-Ph(CN)CC(CN)Ph](PPh$_3$)$_2$ with important bond distances.

TABLE 8

A COMPARISON OF STRUCTURAL PARAMETERS OF SELECTED Pt(olefin)(PPh_3)$_2$ COMPLEXES

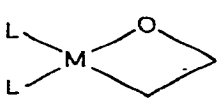
	 [a]	 [b]	 [c]	 [d]
Distances (Å)				
Pt—P(1)	2.295(2)	2.291(9)	2.277(5)	2.298(4)
Pt—P(2)	2.289(2)	2.288(8)	2.296(4)	2.261(4)
Pt—C(1)	2.102(7)	2.12(3)	2.05(2)	2.09(1)
Pt—C(2)	2.113(8)	2.10(3)	2.16(2)	2.17(1)
C(1)—C(2)	1.50(1)	1.49(5)	1.53(4)	1.42(2)
Angles (°)				
P(1)—Pt—P(2)	103.51(9)	101.4(3)	104.4(2)	109.5(1)
P(1)—Pt—C(2)	104.6(2)	111(1)	102.7(7)	105.0(4)
P(2)—Pt—C(1)	110.0(2)	106(1)	110.5(7)	106.9(4)
C(1)—Pt—C(2)	41.7(3)	42(1)	43(1)	38.8(4)
Dihedral Angles (°) [e]				
α [e]	64.1(8)	66.1	—	38
$\beta_{1,2}$	55.2(8)	63.8	—	85(2)
	60.8(9)			
$\gamma_{1,2}$	144.2(7)	141.3	—	150
	138.0(6)			
δ_{1-4}	110.5(5)	—	—	99(1)
	105.3(6)			111(1)
	112.0(7)			
	110.0(6)			
θ	8.9(4)	8.3	—	8.7(7)
ψ	83.2(4)	—	—	—

[a] This paper. Structure determined at −150°C. [b] Ref. 20. [c] Ref. 21. [d] Ref. 22. [e] Angles α—δ, θ, ψ are defined in ref. 19.

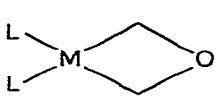
ing in Fig. 5. The C(1)—C(2) olefin bond distance of 1.50(1) Å is elongated from the free olefin, as expected in the π-complex of an electronegative olefin [19]. There is considerable π-backbonding into the π^* orbital of the olefin, induced by the cyano substituents. The P(1)—Pt—P(2) angle at 103.51(9)° and the C(1)—Pt—C(2) angle at 41.7(3)° are typical for platinum(0)—olefin complexes of this type [19]. A comparison of these quantities with those in related structures [20—22] is given in Table 8.

Discussion

Insertion reactions into oxirane rings by zerovalent transition-metal centers can lead to two possible oxametallacyclobutanes:

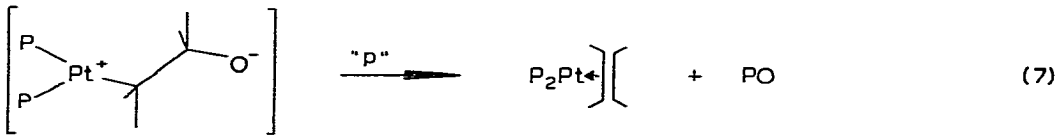


(IV)



(V)

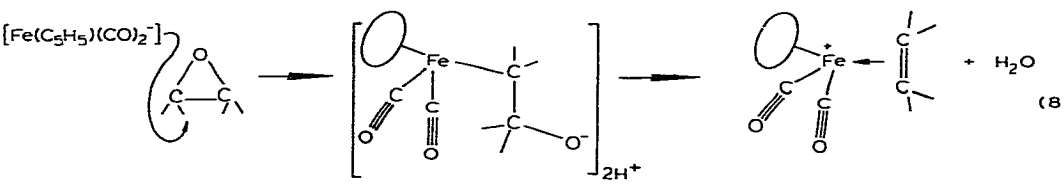
In practice, only isomer IV has been observed; no C—C bond cleavage has been observed in any of the metal-mediated ring-opening reactions. With tetracyano- and tricyanooxiranes, the C—O^- bond is apparently strong enough that this bond will remain intact through a C—C bond rotation and ring closure to the metallacycle after the initial S_N2 attack [2—4]. In the reactions of the phenyl-substituted dicyanooxiranes not only does C—O bond cleavage of one side of the oxirane occur, but a complete scission of the oxygen atom from the two-carbon-atom unit takes place. This cleavage presumably occurs because the phenyl groups weaken the C—O^- bond [23]. The structure of the deoxygenated reaction product of I, Pt[*trans*-Ph(CN)CC(CN)Ph]$(PPh_3)_2$, demonstrates that the *trans*-stereo chemistry of the starting oxirane is retained in the reaction. This is consistent with the S_N2 mechanism; the loss of oxygen from the *trans*-dipolar intermediate would occur before any C—C bond rotation (eq. 7).



(7)

The identity of "P", the phosphine species that does the actual deoxygenation, is still unknown. It has been observed that excess free PPh_3 or PEt_3 will promote the deoxygenation, but the uncertain degree of dissociation of the materials generated upon dissolution of the platinum and palladium starting materials makes this phenomenon difficult to quantify [24].

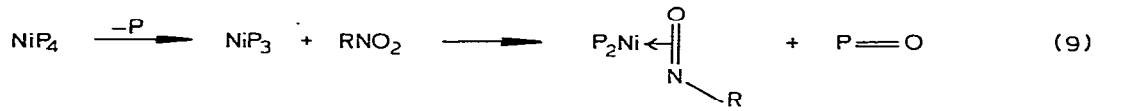
Deoxygenation of oxiranes in the presence of transition-metal species has been noted before. The reaction of $Na[Fe(C_5H_5)(CO)_2]$ with simple oxiranes produces an iron—olefin complex. The ring-opening reaction proceeds by an S_N2 mechanism ($Fe(C_5H_5)(CO)_2^-$ being a very strong nucleophile) and the olefin configuration in the final complex is the same as that of the starting oxirane. The oxygen atom is lost as H_2O after successive protonations of the intermediate, accounting for the oxidation state change to a cationic iron(II)—olefin complex [25] (eq. 8).



(8)

The isomerization of oxiranes by $Mo(CO)_6$ proceeds with the production of minor amounts of deoxygenated olefin by-products [26]. Deoxygenation of the oxirane ring also occurs with the more basic phosphines and phosphites in the absence of a metal, but with PPh_3 and no metal very high temperatures (165 to 170°C) are required [27]. Tributylphosphine and triethylphosphine have been reported to deoxygenate oxirane rings to olefins at 150—175°C [8,28].

Berman and Kochi have reported a similar reaction between d^{10} nickel(0) compounds and nitro compounds; a deoxygenation reaction by the nickel(0) phosphine complex takes place to produce phosphine oxide and a π-nitroso complex of nickel(0) [29] (eq. 9).



An electron transfer from nickel(0) to nitro compound is proposed as the initial reaction step, but the decomposition reaction probably proceeds via a cyclic intermediate.

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