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Rhodium and Iridium Phosphine Olefin Complexes. Phosphorus-31 Nuclear Magnetic Resonance Assignment of Trigonal-Bipyramidal Structures

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The structures of the five-coordinate compounds RhCl(mbp)$_2$ (mbp = Ph$_2$PCH$_2$CH$_2$CH=CH$_2$), RhBr(mbp)$_2$, RhCl(map)$_2$ (map = Ph$_2$POCH$_2$CH=CH$_2$), and RhCl(tpb) (tbp = P(CH$_2$CH$_2$CH=CH$_2$)$_3$) were investigated in solution by infrared and ^{31}P NMR spectroscopy. On the basis of ^{31}P NMR temperature studies, several isomers are observed which, depending on the compound and the temperature, undergo differing degrees of exchange with each other. Four-coordinate isomers of RhCl(mpb)$_2$ and RhBr(mbp)$_2$ are present at 32 °C by infrared analysis although absent at −75 °C by ^{31}P NMR analysis. Comparisons are made between Rh and Ir, Cl and Br, and mbp and map as to their control upon the isomers present in solution.

Introduction

We have recently reported the crystal structure of RhCl(mbp)$_2$ (mbp = Ph$_2$PCH$_2$CH$_2$CH=CH$_2$).[2] It is best described as a distorted trigonal bipyramid containing a phosphorus and a chlorine in apical positions and a phosphorus atom and two olefins in the equatorial plane. The solid-state infrared spectrum is in agreement with such a five-coordinate formulation exhibiting ν(C=C)[3] at 1505 cm^{-1} and no band at 1638 cm^{-1}. Examination of the ir spectrum of this complex in CHBr$_3$ solution, however, reveals both bonded and nonbonded olefin at 1638 and 1508 cm^{-1}, respectively, indicating the presence of both four- and five-coordinate isomers in solution. Correspondingly, the ^{1}H NMR of RhCl(mpb)$_2$ is very complex. No coupling information is extractable between −60 and +80 °C,[5] in contrast to the case of other compounds of mbp (Rh[6], Mo,[7] Pt,[4] Pd[4]), where ^{1}H NMR has been of great utility in identification.

The studies described herein were undertaken both to compare RhCl(map)$_2$ (map = Ph$_2$P(OCH$_2$CH=CH$_2$)) and IrCl(mbp)$_2$ to the aforementioned RhCl(mbp)$_2$ and to test the applicability of ^{31}P NMR to the structural elucidation of the above and related complexes in solution.

Iridium olefin complexes have not received extensive study[8] and few comparisons between rhodium(I) and iridium(I) olefin complexes have been made.[9,10]

Results and Discussion

The complex IrCl(mbp)$_2$ is prepared by the reaction of Ir$_2$Cl$_2$(COT)$_4$ (COT = cyclooctene) with mbp in a 1:4 molar ratio. It is a colorless material that crystallizes as a benzene solvate. The complex RhCl(map)$_2$ is similarly prepared by the reaction of Rh$_2$Cl$_2$(COD)$_2$ (COD = cyclooctadiene) with map in a 1:4 molar ratio. Examination of the infrared spectra of IrCl(mbp)$_2$ and RhCl(map)$_2$ revealed no free olefin in either the solid state or CHBr$_3$ solution, in contrast to RhCl(mbp)$_2$. Bonded ν(C=C) was observed at 1505 cm^{-1} for RhCl(map)$_2$. Bonded ν(C=C) for IrCl(mbp)$_2$ was not observed but was probably obscured by the strong phenyl absorption at 1480 cm^{-1}. A peak corresponding to the parent ion was observed in the mass spectra of both complexes as further confirmation of their proposed formulations. ^{1}H NMR of both compounds revealed complex patterns with a multitude of what could be assigned as vinyl and methylene resonances. The complexity of the ^{1}H NMR of RhCl(mbp)$_2$, RhBr(mbp)$_2$, RhCl(map)$_2$, and IrCl(mbp)$_2$ indicates the possibility of more than one compound or isomer. Examination of the ^{31}P NMR of these complexes was therefore undertaken in the hope of gaining more structural information about these complexes in solution.

Table I. Infrared and ^{31}P NMR Data[a]

	ν(C=C) [Nujol (CHBr$_3$)], cm^{-1}	^{31}P δ,[b] ppm	J values, Hz
RhCl(mbp)$_2$	1505 (1638, 1505)	−74.9 (III, P$_E$)	$^1J_{Rh-P_E}$ = 145
		−26.8 (III, P$_A$)	$^1J_{Rh-P_A}$ = 111 $^2J_{P_A-P_E}$ = 26.8
RhBr(mbp)$_2$	1505 (1639, 1505)		
RhCl(map)$_2$	1505 (1505)	−156.2 (III, P$_E$)	$^1J_{Rh-P_E}$ = 146
		−139.8 (III, P$_A$)	$^1J_{Rh-P_A}$ = 116 $^2J_{P_A-P_E}$ = 21.0
Rh$_2$Cl$_2$(mbp)$_2$	1488 (1488)	−68.6, −69.6 (I and/or II)	$^1J_{Rh-P}$ = 188 $^1J_{Rh-P}$ = 189
IrCl(mbp)$_2$	<1500 (<1500)	−6.7 (III, P$_A$)	$^2J_{P_A-P_E}$ = 11
		−29.9 (III, P$_E$)	
RhCl(tbp)		−134	$^1J_{Rh-P}$ = 120

[a] ^{31}P data given for isomers that can be unequivocally assigned; for others see Results and Discussion. [b] Relative to 85% H$_3$PO$_4$, downfield shifts being negative.

^{31}P Studies. Rh$_2$Cl$_2$(mbp)$_2$. Throughout this work a recurring question is the magnitude of change necessary in a molecule for magnetically nonequivalent atoms to exhibit observably different chemical shifts. It is hoped that this study will provide a partial answer to that question. The ^{31}P NMR spectrum of Rh$_2$Cl$_2$(mbp)$_2$ (Figure 2) indicates the presence of two isomers in a 2:1 ratio. One can envision "cis" and "trans" isomers depicted in Figure 1 by structures II and I, respectively. If one assumes that the olefin adopts a configuration perpendicular to the Rh–P bond,[11] then three isomers are possible for both I and II. Isomers a and b are enantiomorphs and thus result in phosphorus nuclei that are magnetically equivalent. A random distribution of the three isomers should produce resonances in the ratio of 2:1 for either I or II. One cannot say with certainty whether I, II, or one isomer of each is being observed; however, if steric interactions are considered, I would be favored, particularly in the bent configuration known for several similar rhodium dimers.[12] Cooling the solution to −75 °C revealed no change in the ratio of the isomers. The chemical shifts (Table I), which are considerably downfield from those observed for Rh$_2$Cl$_2$(P-(p-tol)$_3$)$_4$,[13] have been discussed previously[14] and explained on the basis of a chelation effect, Δ_R, which is also observed for diphosphines,[14] ortho-metalated phosphines,[14] and ortho-metalated phosphites.[15]

RhCl(mbp)$_2$. At 32 °C the ^{31}P spectrum of RhCl(mbp)$_2$ exhibits a broad resonance centered at −50 ppm. At −75 °C the spectrum (Figure 2b) consists of two doublets centered at −74.9 ppm and two doublets centered at −26.4 ppm in addition to a broadened multiplet at −50 ppm. The former resonances can be attributed to an isomer of III. Four isomers are

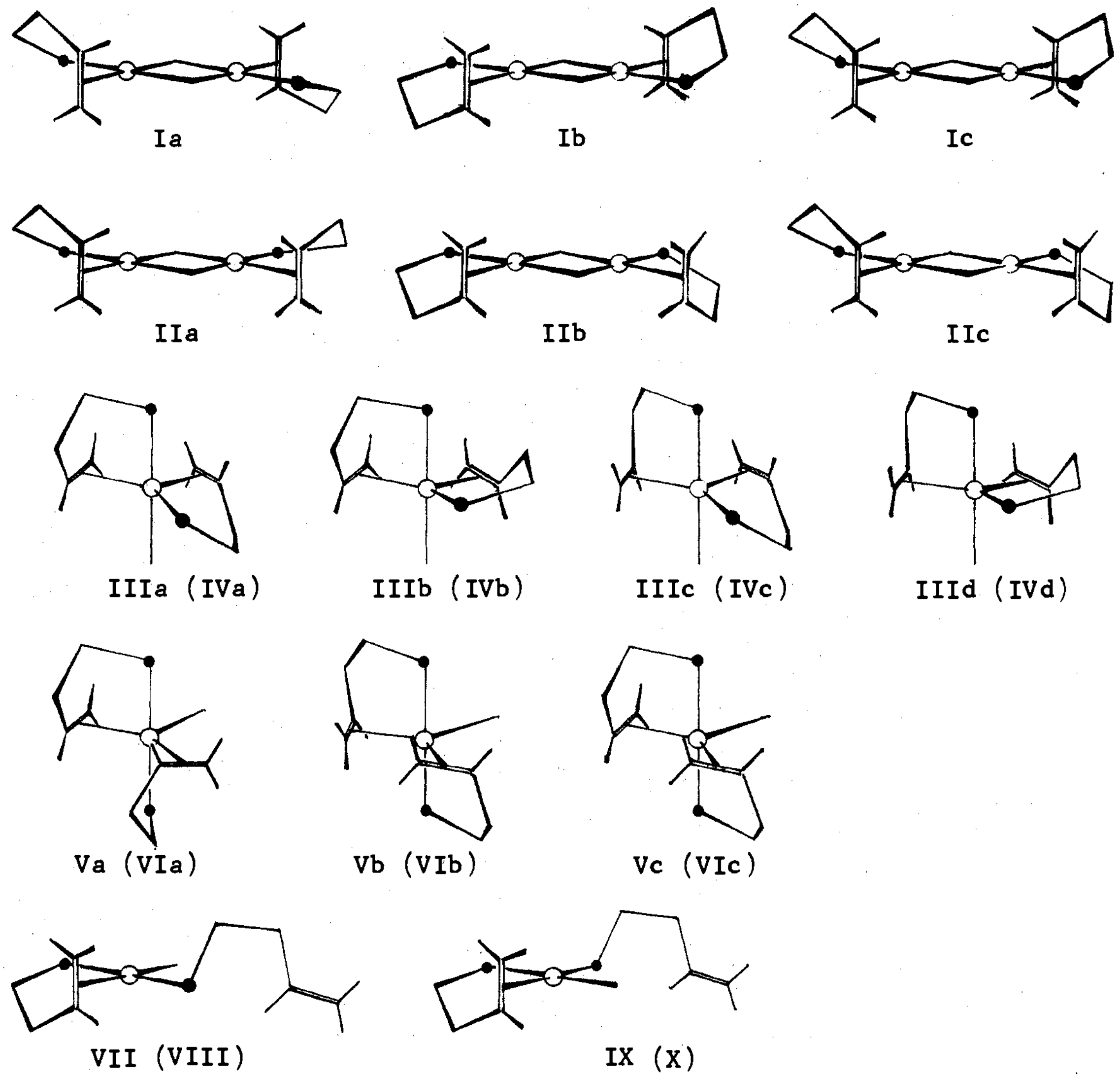

Figure 1. Possible structures of phosphine-olefin complexes [phenyls have been omitted for clarity; ● = P; ○ = Rh (or Ir)].

possible; isomer IIIc is the one observed in the crystal structure determination.[2]

We assign the resonance at −26.4 ppm to an axial phosphorus, $J_{\text{Rh}-\text{P}_\text{A}} = 110.7$ Hz, and that at −74.9 ppm to an equatorial phosphorus, $J_{\text{Rh}-\text{P}_\text{E}} = 145.0$ Hz, with reference to the results of Meakin and Jesson[16,17] on five-coordinate rhodium phosphite complexes and the coupling observed for the axial phosphorus in RhCl(tbp), $^1J_{\text{Rh}-\text{P}} = 120$ Hz (see below).

The broadened multiplet at −50 ppm may be due to isomers of V still undergoing exchange at −75 °C.

IrCl(mbp)$_2$. At 32 °C the spectrum in Figure 3 is consistent with the presence of IV with resonances centered at $\delta_{\text{P}_\text{A}}$ −6.6 ppm and $\delta_{\text{P}_\text{E}}$ −29.5 ppm with a cis $^2J_{\text{P}_\text{A}-\text{P}_\text{E}} = 11$ Hz. In contrast to the spectrum of RhCl(mbp)$_2$, the broad resonance (30%) at δ −22.2 ppm sharpens into three resonances at −75 °C. The resonance at δ −19.3 ppm is consistent with structure VIa or b where the phosphorus nuclei are equivalent and the resonances at −23.9 and −22.0 ppm are consistent with VIc where the phosphorus nuclei are nonequivalent and result in an AB spectrum. The outer "wings" of the AB pattern were not observed.[18]

The presence of isomers such as VIII and X can be ruled out. It has been shown[14] that chelated phosphine–olefin ligands exhibit chemical shifts ca. 25 ppm downfield relative to unchelated ligands. This eliminates the assignment of the resonances at −23.9, −22.0, and −19.3 ppm to VIII or X. An alternate assignment of the phosphorus resonances at δ −6.6 and −29.5 ppm requires $^2J_{\text{P}-\text{P}} = 11$ Hz. This is not reasonable for isomer VIII where analogous compounds, *trans*-IrClCO(PR$_3$)(PR'$_3$), have $^2J_{\text{PP}}$ values of ~350 Hz,[19] but assignment of structure X cannot be completely ruled out since

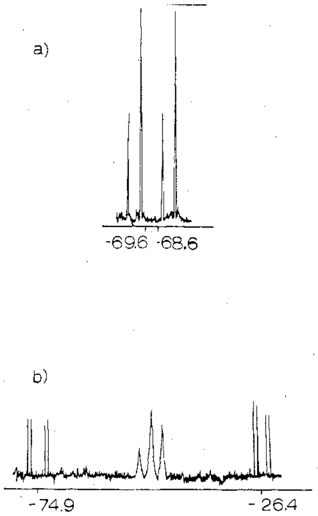

Figure 2. (a) ^{31}P NMR of Rh$_2$Cl$_2$(mbp)$_2$ at 32 °C in CH$_2$Cl$_2$. (b) ^{31}P NMR of RhCl(mbp)$_2$ at −75 °C in CH$_2$Cl$_2$.

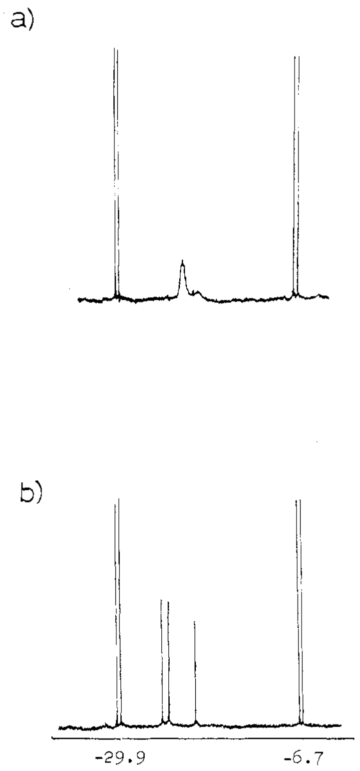

Figure 3. ^{31}P NMR of IrCl(mbp)$_2$ in CH$_2$Cl$_2$: (a) 32 °C; (b) −75 °C.

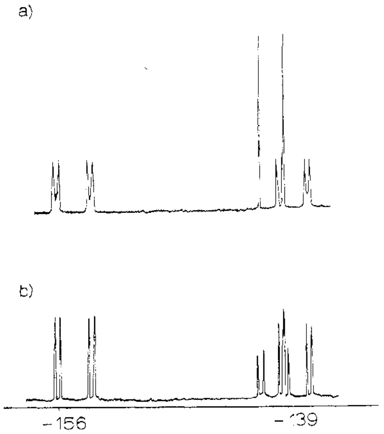

Figure 4. ^{31}P NMR of RhCl(map)$_2$ in CH$_2$Cl$_2$: (a) 32 °C; (b) −75 °C.

no cis $^2J_{\text{P-P}}$ values are available. The presence of such isomers is improbable due both to the lack of the free olefin frequencies in the solution ir spectrum at 32° and to the information derived from RhCl(map)$_2$ and RhBr(mbp)$_2$ below.

RhCl(map)$_2$. The ^{31}P NMR of RhCl(map)$_2$ at 32 °C reveals an isomer of III: $\delta_{\text{P}_\text{A}}$ −139.8 ppm and $\delta_{\text{P}_\text{E}}$ −156.2 ppm with $^1J_{\text{Rh-P}_\text{A}}$ = 116 Hz, $^1J_{\text{Rh-P}_\text{E}}$ = 146 Hz, and $^2J_{\text{P}_\text{A}\text{-P}_\text{E}}$ = 21 Hz (Figure 4). In addition, an apparent doublet is observed as 50% of the total intensity. Upon cooling of the compound to −75 °C, 78% of the area is now in the form of an isomer of III while the "doublet" has decreased to 22% and has become two "doublets". These two "doublets" can be explained by the presence of two isomers of V. Either "doublet" can be attributed to isomer Va, Vb, or Vc. If Va and/or Vb are assumed, reasonable $^1J_{\text{Rh-P}}$ values of 105 Hz are obtained. However, either "doublet" might be an ABX spectrum due to Vc with coupling such that the wings are not observable. The measured peak width at half-height for both sets of "doublets" is 6 Hz.

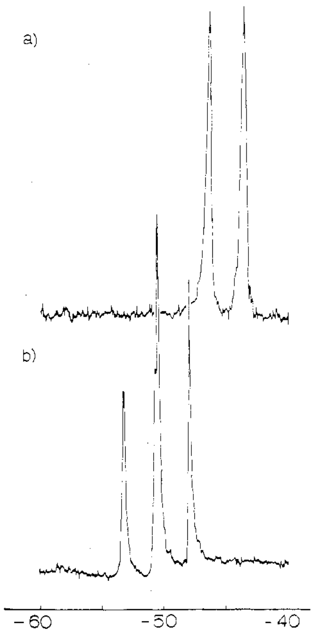

Figure 5. ^{31}P NMR of RhBr(mbp)$_2$ in CH$_2$Cl$_2$: (a) 32 °C; (b) −75 °C.

RhBr(mbp)$_2$. At 32 °C the ^{31}P spectrum of RhBr(mbp)$_2$ exhibits a "doublet" at −45 ppm (Figure 5) Upon cooling of the compound, four signals are observed centered at −50 ppm. The shifting of the center of the resonances indicates the presence of an isomer at 32 °C which is not present in an observable quantity at −75 °C. It should be noted that the change from Cl to Br has caused the disappearance of an isomer of III and the "freezing out" of an isomer of V whereas the ^{31}P NMR of RhCl(mbp)$_2$ indicated the presence of an isomer of III and the exchange of isomers other than III at −75 °C. Again, the presence of four-coordinate isomers at −75 °C is ruled out due to the absence of resonances which could be attributed to chelated and unchelated ligands at −75 °C. Their presence in the exchanges occurring at 32 °C is plausible since VII would be expected at ca. −29 ppm[19] and free olefin is observed at 1639 cm^{-1} in the CHBr$_3$ solution ir spectrum at this temperature. The two doublets can be explained on the basis of the presence of two isomers of V. As in the case of RhCl(map)$_2$ if either "doublet" is due to Va or Vb, then one obtains $^1J_{\text{Rh-P}}$ of 108 Hz, or if one of the "doublets" is due to Vc, an ABX pattern must be assumed.

RhCl(tbp). Examination of the ^{31}P spectrum of RhCl(tbp) revealed a typical $^2J_{\text{Rh-P}}$ of 120 Hz and an unexpectedly low δ_P value of −134 ppm. This extremely large coordination chemical shift can be explained in terms of a ring contribution, Δ_R, to the chemical shift.[14] This effect is much larger than previously observed due to the fact that the phosphorus nuclei are involved in tetradentate chelation thus causing 3 times the "expected" Δ_R value of 21–30 ppm.[14] This phenomenon has been recently observed in tetradentate chelation of the ligand P(CH$_2$CH$_2$PPh$_2$)$_3$.[20]

Rotation Possibilities and Preferred Conformations within Isomers. When examining the isomeric possibilities one must recall that it has been shown[7] that the olefin can undergo a restricted rotation of ca. 90° from a configuration with the olefin perpendicular to one with the olefin parallel to the metal–phosphorus bond but further rotation (leading to isomerization) without bond breakage is not possible (Figure 6).

The most favorable orientations for olefins are those that allow maximum overlap between the filled metal d orbitals and the antibonding orbitals on the carbon atoms. An olefin

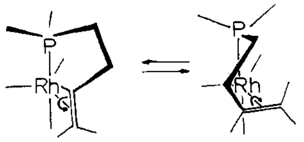

Figure 6. Restricted olefin rotation for P_A of IIIa.

in the equatorial plane of a trigonal bipyramid can accept electron density from the $d_{x^2-y^2}$ or d_{xy} orbitals and if perpendicular to the plane from the d_{xz} or d_{yz} orbitals of the metal. When this latter set of orbitals is also involved in bonding to the apical atoms, the planar configuration for the olefin appears more favorable for back-bonding. Crystallographic results on RhCl(tbp)[21] and RhCl(mbp)$_2$[1] support these assumptions. Others[22] have discussed site preference in pentacoordinate molecules.

Attempted Reaction of IrCl(mbp)$_2$. Hydrogen was found to hydrogenate RhCl(mbp)$_2$ in methanol producing a deep red solution.[23] Interaction of a methanol or benzene solution of IrCl(mbp)$_2$ and H_2 over extended periods failed to hydrogenate the complex. No color change was noted and the ^1H NMR of the solution indicated the presence of only the starting complex. Interaction of IrCl(mbp)$_2$ with PPh_3 also failed to induce replacement of the olefins.

Experimental Section

Infrared spectra were recorded on a Perkin-Elmer 621 spectrometer. Proton magnetic resonance spectra were recorded on a Varian 220 spectrometer. ^{31}P spectra were obtained in CH_2Cl_2 at 40.5 MHz on a Varian XL-100 spectrometer as described earlier.[19]

Molecular weights were determined in $CHCl_3$ on a Hewlett-Packard 302 vapor pressure osmometer. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. All reactions were carried out under argon and all solvents were deaerated prior to use. The ligands mbp[24] and map[24] and the complexes Rh_2Cl_2(mbp)$_2$[5] and RhCl(mbp)$_2$[5] were prepared according to published methods.

(a) Reaction of [IrCl(COT)$_2$]$_2$ with mbp. The addition of mbp (0.145 ml) in 5 ml of dry benzene to a suspension of [IrCl(COT)$_2$]$_2$ (0.135 g) in 10 ml of dry benzene resulted in a clear lemon yellow solution. The reaction was stirred at room temperature for 2 h. Addition of 5 ml of isooctane and subsequent concentration by vacuum to ca. 10 ml resulted in the precipitation of a white crystalline material. The complex was collected by filtration, recrystallized from benzene/hexane, and vacuum-dried. The yield of IrCl(mbp)$_2\cdot C_6H_6$ was typically 75–85%. Anal. Calcd for $C_{38}H_{40}ClIrP_2$: C, 56.29; H, 5.15. Found: C, 56.78, H, 5.06.

(b) Reaction of Rh_2Cl_2(COD)$_2$ with map. The addition of map (0.38 ml) in 5 ml of dry ether to a suspension of Rh_2Cl_2(COD)$_2$ (0.20 g) in 20 ml of dry ether resulted in a clear solution. RhCl(map)$_2$ soon precipitated and was filtered, washed with dry ether, and dried. The yield was typically 65–75%. Anal. Calcd for $C_{30}H_{30}ClIrO_2P_2$: C, 58.00; H, 4.82; P, 9.98. Found: C, 58.12; H, 4.97; P, 9.82.

Registry No. RhCl(mbp)$_2$, 56629-85-7; RhBr(mbp)$_2$, 60362-96-1; RhCl(map)$_2$ (isomer III), 60326-09-2; RhCl(map)$_2$ (isomer V), 60362-97-2; Rh_2Cl_2(mbp)$_2$, 55074-24-3; IrCl(mbp)$_2$ (isomer IV), 60326-10-5; IrCl(mbp)$_2$ (isomer VI), 60362-98-3; RhCl(tbp), 60362-99-4; ^{31}P, 7723-14-0; [IrCl(COT)$_2$]$_2$, 12246-51-4; Rh_2Cl_2(COD)$_2$, 12112-67-3.

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