Synthesis and X-ray Crystal Structure of a Unique Rhodium(I) Phosphine Complex: A Novel Intermolecular Ring Closure To Produce a Bidentate Phosphorus Alkyl Bound Ligand[†]

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Summary: Methane, isobutene, and a novel phosphorus–carbon bound rhodium(I) complex are the products of the reaction of (1,5-cyclooctadiene)(2-methylallyl)rhodium(I) with bis[bis(trimethylsilyl)methyl]phosphine. The reaction with di-*tert*-butylphosphine is also discussed.

The reaction of (1,5-cyclooctadiene)(2-methylallyl)rhodium(I), $[Rh(\eta^4\text{-}1,5\text{-COD})(\eta^3\text{-}2\text{-Me-C}_3H_4)]$, **1**, with bis[bis(trimethylsilyl)methyl]phosphine, **2**, in hexane at 65 °C results in the production of methane, isobutene, and (η^2-3,3,5,5-tetramethyl-*syn*-2-(trimethylsilyl)-*anti*-6-(trimethylsilyl)-1-phospha-3,5-disilacyclohex-4-yl)(η^4-1,5-cyclooctadiene)rhodium(I), **3**, a novel phosphorus–carbon bound rhodium(I) complex that still contains the COD group (Scheme I).[1]

The yellow crystalline complex **3** is very soluble in aromatic and hydrocarbon solvents but can be recovered in 80% yield by cooling a saturated hexane solution to −30 °C. The complex melts at 182 °C (sealed capillary) with subsequent darkening. The unusually high thermal stability of **3** may be due to the lack of β-hydrogen that precludes the usual β-elimination pathway of σ-bound rhodium alkyls.

The volatile products of the reaction between **1** and **2** were analyzed by a Finnigan 3200 GC/MS equipped with a 30-m column. The presence of isobutene was detected. We believe the other product is CH_4 due to the presence of a very volatile gas that condenses at about −160 °C and freezes at near liquid N_2 temperatures when separated by trap-to-trap distillation. The presence of CH_4 is also supported by the reaction stoichiometry.

The reactions of **1** with various monodentate and bidentate phosphites and phosphines have been examined in a number of recent publications.[4-6] In sharp contrast to our results, the addition of the phosphorus ligand(s) has resulted in the loss of the COD group to produce some interesting four- or five-coordinate rhodium(I) complexes. These complexes characteristically have the phosphorus bases arranged in a cis geometry. The large steric bulk of the phosphine **2** may account for the difference in reactivity and the products obtained. Further evidence for the size of **2** is that the complex *trans*-$[Rh(CO)Cl(PH\{CH(SiMe_3)_2\}_2)_2]$ is the exclusive product (^1H NMR, ^{31}P NMR, and X-ray data),[7] when $[Rh(CO)_2Cl]_2$ is treated with an excess of **2**.

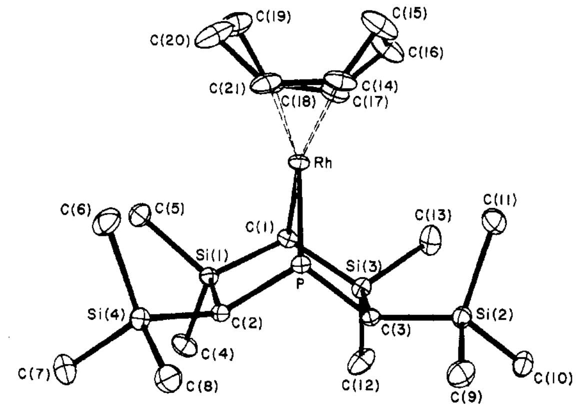
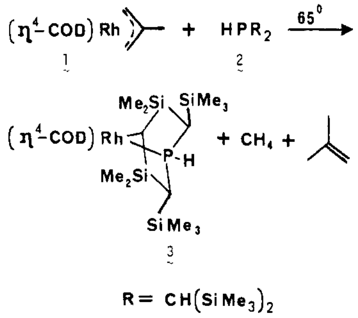


Figure 1. ORTEP drawing of **3**.

Scheme I



The mechanism of the reaction in Scheme I is not known, but it may initially involve a complex that contains COD, phosphine, and a η^3-methylallyl,[8,9] followed by a Lewis base promoted π–σ transformation to produce a η^1-methylallyl species.[10] The η^1-methylallyl group may assist in a hydrogen transfer from a γ-carbon[11] to yield isobutene. The fact that these reactions are known does not preclude a radical mechanism or other pathway.

Intramolecular metalation reactions involving aromatic carbon in phosphines have been extensively studied over the past 15 years.[12,13] Corresponding reactions of purely aliphatic phosphines have been the subject of much fewer articles.[14-17] These metalation reactions are thought to be promoted by bulky substituents on phosphorus and the formation of four- and five-membered rings.

The structure of **3**, as determined by X-ray crystallography,[18] is depicted in Figure 1. Some important bond

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[†] No reprints available.

[1] All operations were carried out in a Vacuum Atmosphere HE-43-2 drybox, in a conventional vacuum system or by using standard Schlenk techniques. Bis{bis(trimethylsilyl)}methylphosphine,[2a,b] di-*tert*-butylphosphine,[3] and Rh(COD)(2-Me-C_3H_4)[4] were prepared by standard literature procedures. All solvents used were dried, distilled, and degassed prior to use.

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[9] We have recently prepared the complex $Ir(\eta^3\text{-}C_3H_5)(\eta^4\text{-}1,5\text{-COD})[HP(t\text{-}C_4H_9)_2]$.

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Table I. Selected Bond Distances (Å) and Angles (deg) for 3

(a) Bond Distances

Rh-P	2.279 (1)	P-(H1P)	1.40 (3)	Si(3)-C(3)	1.920 (3)
Si(2)-C(3)	1.886 (3)	Rh-C(1)	2.159 (2)	C(1)-H(1)	0.88 (3)
Si(3)-C(1)	1.849 (3)	P-C(3)	1.827 (2)	P···C(1)	2.778 (3)
Si(3)-C(12)	1.881 (2)				

(b) Bond Angles

Rh-P-C(3)	107.1 (1)	P-C(3)-Si(2)	115.2 (1)	Rh-P-C(2)	107.5 (1)
C(1)-Si(3)-C(3)	104.9 (1)	Rh-C(1)-Si(3)	102.8 (1)	C(2)-P-C(3)	103.9 (1)
C(3)-Si(3)-C(12)	106.9 (1)	C(14)-Rh-C(17)	81.7 (1)	C(1)-Si(3)-C(12)	116.3 (1)
C(3)-Si(3)-C(13)	112.9 (1)	C(17)-Rh-C(18)	36.4 (1)		

distances and angles are presented in Table I.

The unusual bidentate, heterocyclic ligand can be viewed as a *cis*-bicyclo[2.2.1]heptane (norbornane) analogue that has a rhodium atom at the bridgehead position.

Formation of **3** involves the activation of Rh–C, C–Si, and C–H bonds as well as the elimination of CH_4 and isobutene. The drive to form the new Rh–P and Rh–C bonds is assisted by the increased entropy of the products and the ease at which the volatile products can be removed. The production of **3** results in a buildup of ring strain. Considerable distortion occurs at C(1), C(2), and C(3) where the Si(1)–C(1)–Si(3), Si(1)–C(2)–Si(4), and Si(3)–C(3)–Si(2) angles are 117.6 (1)°, 121.2 (1)°, and 120.6 (1)°. The Rh–C(1)–Si(1), P–C(2)–Si(1), and P–C(3)–Si(3) angles are 100.3 (1)°, 101.5 (1)°, and 101.7 (1)°. These angles differ widely from those of a tetrahedral carbon (109.5°). The Si(1)–C(2) and Si(3)–C(3) bond distances are very long (~1.92 Å), which provides further evidence for ring strain. The rhodium atom is in a distorted square-planar geometry with the P–Rh–C(1) angle being 77.5(1)°. The compression of this angle from the normal square-planar angle of 90° is related to the length of the Si(1)–C(2) and Si(3)–C(3) bonds. Wider angles would require additional stretching of these bonds, and they are already lengthened considerably (1.92 Å) from that of a typical Si–C bond (1.85 Å).

The cyclooctadiene group exists in the expected boat configuration with the C(14)–C(21) and C(17)–C(18) bond distances of 1.381 (4) Å and 1.378 (5) Å, respectively. The four olefinic carbon to rhodium bond distances range from 2.157 (2) to 2.217 (3) Å.

The X-ray structure of **3** agrees with the spectroscopic data obtained:[19] ^1H NMR (200 MHz, C_6D_6, ppm) 5.00, 4.26 (br s, 4 H, COD vinyl protons), 4.12 (d of d, 1 H, $^1J_{P-H}$ = 292.3 Hz, $^3J_{PH-CH}$ = 5.5 Hz, P–H), 2.18, 1.98 (br m, 8 H, exo and endo methylene protons of COD), 0.49, 0.40 (s, 12 H, $SiMe_2$), 0.30 (s, 18 H, $SiMe_3$); $^{31}P\{^1H\}$ NMR (81 MHz, C_6D_6, ppm) −15.2 (d, $^1J_{Rh-P}$ = 152.3 Hz).

The reaction of di-*tert*-butyl phosphine with **1** at 25 °C in benzene-d_6 produces a number of products. We have monitored the reaction by ^{31}P NMR and witnessed the immediate disappearance of the free phosphine peak at +20 ppm with the subsequent production of many peaks downfield. A number of these peaks can be assigned to phosphine-bound rhodium species as they exhibit $^1J_{Rh-P}$ of between 110 and 190 Hz and have large $^1J_{P-H}$ (~300 Hz). We have obtained colorless crystals from cooling hexane solutions and will present their structures in a full account of this work.[21]

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Supplementary Material Available: Tables of bond distances and angles, structure factors, and positional and thermal parameters (38 pages). Ordering information is given on any current masthead page.

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(18) X-ray diffraction data for $RhC_{21}H_{44}PSi_4$, **3**: crystal system, triclinic; space group $P\bar{1}$, No. 2; cell dimensions at 140 K; a = 10.554 (2) Å, b = 11.239 (2) Å, c = 13.189 (2) Å; α = 103.00 (1)°, β = 101.27 (1)°, γ = 108.09 (2)°; V = 1388.3 (5) Å^3; Z = 2; μ(Mo Kα) = 8.38 cm^{-1}; crystal size = 0.22 × 0.27 × 0.37 mm; yellow prisms; ρ^{298K}(exptl) = 1.279 g·cm^{-3}, ρ^{140K}(calcd) = 1.30 g·cm^{-3}; diffractometer, Syntex $P2_1$; radiation, graphite-monochromatized Mo Kα; data collection temperature, 140 K; scan range, 1°; scan speed, 15° min^{-1}; 2θ range 0–55°; reflections collected, 6349 unique, 5807 with $F_o > 3\sigma(F_o)$. All calculations were carried out on a Data General ECLIPSE computer using the SHELXTL program system. The atomic form factors including anomalous scattering were from ref 14. The data was corrected for absorption. The structure was solved by a combination of Patterson and difference Fourier techniques. All of the hydrogen atoms were located and refined: R = 0.031 with non-hydrogen atoms assigned anisotropic and hydrogen atoms assigned isotropic thermal parameters; R_w = 0.027, weighting scheme $1/\sigma^2(F)$.

(19) ^1H and ^{31}P NMR data were obtained on a NT-200 spectrometer operating at 200 and 81 MHz. All samples were run in freshly dried and distilled benzene-d_6. 85% H_3PO_4 was used as an external standard for the ^{31}P spectra.

(20) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, 1962; Vol. 3.

(21) One of the crystalline products of obtained is Rh(η^4-1,5-COD)(η^3-2-Me-C_3H_6)[HP(t-C_4H)$_2$].

Synthesis of Trinuclear Alkylidyne Complexes from Dinuclear Alkyne Complexes and Metal Hydrides. CIDNP Evidence for Vinyl Radical Intermediates in the Hydrogenolysis of These Clusters

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Summary: Treatment of dicobalt alkyne complexes $Co_2(CO)_6(HCCR)$ (R = alkyl, aryl) with H_2 and $Co_2(CO)_8$ or $CpMo(CO)_3H$ leads to μ_3-alkylidyne complexes with molecular formula $Co_3(CO)_9CCH_2R$ and $CpMo(CO)_2Co_2(CO)_6CCH_2R$, respectively, in high yield and purity. Hydrogenation of these clusters occurs under mild conditions (60–90 °C, benzene solution, 3–4 atm of H_2) and gives olefins, paraffins, and carbonyl compounds. A radical pathway for the hydrogenolyses is suggested by the observation of CIDNP in the olefinic product from some of the trinuclear clusters. Isotope labeling studies on the reaction of $Co_3(CO)_9CCH_2C(CH_3)_3$ (**2**) with H_2 are consistent with the intervention of vinyl radical intermediates.

Although metal–carbon bond hydrogenolysis is an important step in many catalytic processes, relatively few direct mechanistic investigations of this reaction exist.[1] We have undertaken a study of homogeneous reactions of trinuclear alkylidyne complexes with hydrogen to inves-