Interaction of {2,6-Bis[(di-*tert*-butylphosphino)methyl]phenyl}rhodium(I) with Hydrocarbons. X-ray Molecular Structure of {2,6-Bis[(di-*tert*-butylphosphino)methyl]phenyl}chlorohydridorhodium(III)[1]

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The complex $[\mathrm{ClRhH\{P(}t\text{-}\mathrm{Bu)_2CH_2C_6H_3CH_2P(}t\text{-}\mathrm{Bu)_2\}]}$, 1, with orthorhombic space group $Pc2_1n$ has cell dimensions $a = 7.879$ (3) Å, $b = 14.388$ (4) Å, $c = 22.868$ (5) Å, $V = 2592.4$ (12) Å^3, and $Z = 4$. Complex 1 can be dehydrohalogenated with $\mathrm{NaN(SiMe_3)_2}$ to give an exceedingly reactive 14-electron species, $[\mathrm{Rh\{P(}t\text{-}\mathrm{Bu)_2CH_2C_6H_3CH_2P(}t\text{-}\mathrm{Bu)_2\}]}$, 3, which interacts with aromatic and aliphatic hydrocarbons. Adducts of 3 can be formed with hydrogen, carbon monoxide, and ethylene. Treatment of 1 with the ylide $^-\mathrm{CH_2{-}PMe_3}^+$ gave an adduct with a rhodium–carbon bond.

Introduction

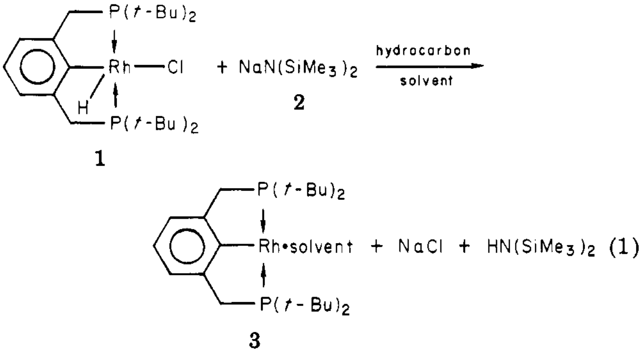
Saturated hydrocarbons are among the most abundant of petrochemicals, but they are the least responsive to selectivity and reactivity by chemical reagents.[2] A challenging aspect of organometallic chemistry is to make these compounds economically attractive in chemical synthesis by using the versatile reaction nature of the carbon–metal bond. Metalation of hydrocarbon C–H bonds by transition-metal complexes followed by treatment with reactive substrates offers a unique approach in obtaining the desired selectivity and reactivity.[3-7]

One possible way of promoting C–H metalation is to synthesize coordinatively unsaturated complexes with bulky groups around the metal atom.[8] This paper describes the synthesis of a 14-electron rhodium complex stabilized by ligands with high steric demand and its remarkable reactivity with aromatic and aliphatic hydrocarbons.

Results and Discussion

Interaction of $[\mathrm{ClRhH\{P(}t\text{-}\mathrm{Bu)_2CH_2C_6H_3CH_2P(}t\text{-}\mathrm{Bu)_2\}]}$, 1, with $\mathrm{NaN(SiMe_3)_2}$, 2.

The X-ray molecular structure of 1[9] (Figure 1) shows a cluster of *tert*-butyl groups around the central rhodium atom. We considered that such a sterically hindered complex could be dehydrochlorinated by a very basic reagent of low nucleophilicity such as $\mathrm{NaN(SiMe_3)_2}$, 2, to form compound 3, a 14-electron species[10] (eq 1). Subsequent experiments confirmed this idea. Treatment of 1 with 2 in benzene, pentane, octane, or cyclohexane for various time intervals up to 48 h followed by filtration of solids (NaCl) and vacuum solvent removal gave an extremely oxygen-sensitive yellow-brown solid. Evidence from IR and ^{1}H, ^{13}C, and ^{31}P NMR data (vide infra) on this product suggested the presence of species 3. However, additional bands and resonances in the IR and NMR spectra indicated that something more than dehydrochlorination had occurred. New ν(RhH) infrared absorption bands were observed at 2136 and 1940 cm^{-1} while RhH resonances were observed at δ −26.0 in the ^{1}H NMR spectra. When the product was redissolved in a deuterated solvent or when the reaction was performed in a deuterated solvent, e.g., benzene-d_6 or cyclohexane-d_{12}, the solid isolated showed IR bands at 1388 cm^{-1} for ν(RhD) along with the usual ν(RhH) bands as well as RhD resonances at δ −27.0 in the ^{2}H NMR spectrum. From these results it was apparent that cyclometalation involving *tert*-butyl groups and attack on hydrocarbon solvents to give rhodium hydride moieties 4 and 5 (Scheme I) had taken place. We do not have any direct evidence



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[1] Presented at the 1980 Biennial Inorganic Chemistry Symposium, Guelph, Ontario, Canada, June 1980, the International Conference on Phosphorus Chemistry, Durham NC, June 1981, the First International Conference of the Platinum Group Metals, Bristol, England, August 1981, and the Pacific Coast Conference on Chemistry and Spectroscopy, Anaheim, CA, Oct 1981.

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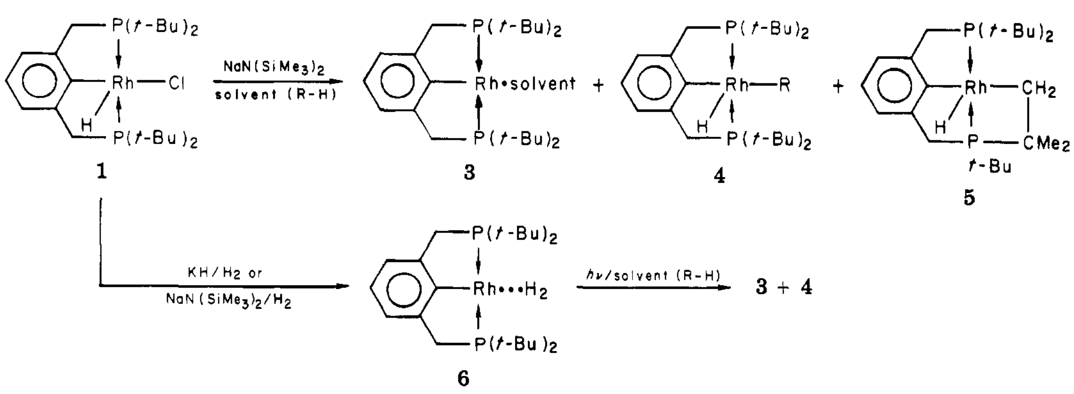
Scheme I. Reaction Pathways for [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$]



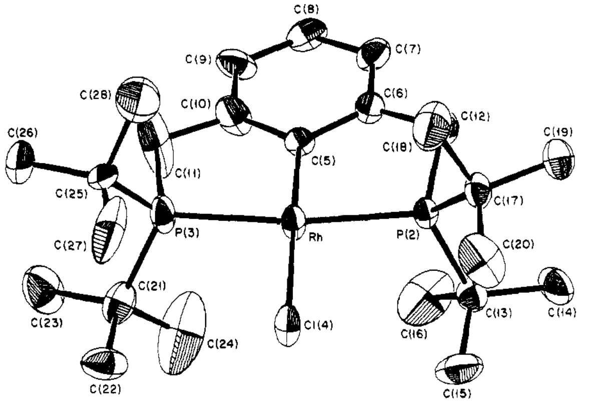


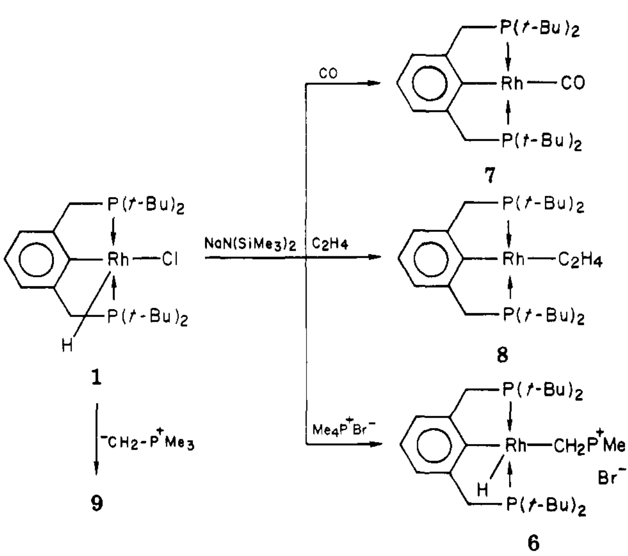
Figure 1. ORTEP drawing of [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$] with ellipsoids of 50% electron density probability. The hydrogen atoms have been omitted for clarity.

for solvent in species **3** except to suggest that a very loosely bonded molecule may exist.[12] Further verification of these reactions were obtained from experiments with the perdeuterio-*tert*-butyl analogue of **1**. Treatment of **1** (t-Bu-d_9)$_4$ with $NaN(SiMe_3)_2$ in a deuterated solvent gave a product with only ν(RhD) bands at 1390 cm^{-1} and ^{2}H NMR resonances at δ −24.0. For the reaction of **1** (t-Bu-d_9)$_4$ with **2** in a nondeuterated solvent, there was IR and NMR spectral evidence for the concurrent presence of RhH and RhD moieties.

We have found the $^{31}P\{^1H\}$ 202-MHz spectrum of the crude reaction mixture to be particularly useful in identifying the species labeled **3**, **4**, and **5** in Scheme I.[11] For instance: the major $^{31}P\{^1H\}$ doublet resonance at δ 81.4 was assigned to **3**;[12] successively smaller doublet resonances at δ 75.2 and 73.5 were assigned to **4**; and the very small pairs of doublet resonances at δ 72.0 and 93.0 represent the inequivalent phosphorus atoms of **5**. We attribute the doublet resonances of **4** to the presence of both equatorial and axial isomers.

Evidence for species **3** and **4** has also been obtained from products generated by photolysis of the dihydride **6** in the appropriate solvent. As illustrated in Scheme I, **6** may be prepared from dehydrohalogenation of **1** in the presence of hydrogen gas. Under UV light, **6** loses H_2, which is detectable by mass spectroscopy, to give species **3** and **4**. Photolysis of **6** in C_6D_{12} gave product **4** with a deuterated cyclohexyl group bonded to the rhodium. The ^{2}H NMR spectrum of this product showed a resonance at δ 0.04 with a ^{2}H solvent and natural abundance *tert*-butyl resonance at δ 1.38; the $^{13}C\{^1H\}$ NMR spectrum showed the α-carbon atom as a triplet at δ 2.99 with J_{PC} = 9.5 Hz. We were not able to detect **5** under the photochemical conditions nor species like Rh(H)D or RhD_2 which could arise from β-elimination of organic groups bonded to rhodium or hydrogenolysis of the Rh–C bond.

Scheme II. Reaction Pathways for [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$] with Ethylene, Hydrogen, Carbon Monoxide, and Methylenetrimethylphosphorane



Scheme II shows that ethylene and carbon monoxide form complexes with **3**. ^{1}H NMR spectroscopy of the ethylene adduct showed no coupling of the ethylene hydrogen atoms to rhodium or phosphorus presumably because of rapid equilibration.[13]

We have also studied the interaction of $^-CH_2–PMe_3^+$ with **1**. There are two ways $^-CH_2–PMe_3^+$ can interact with **1**, namely, substitution of the chlorine atom can give **9** or the phosphorane can act as a powerful base and dehydrochlorinate **1** presumably to give **3** which then interacts with the C–H bond of Me_4P^+Br to form **9**. Scheme II shows that **9** can be formed by both pathways although we are uncertain as to whether these occur simultaneously. Axial and equatorial adducts of $^-CH_2–PMe_3^+$ appeared as

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[11] The assignments of ^{31}P NMR spectra were based on the assumption that species like **1** would have small J_{RhP} coupling constants, i.e., 114 Hz, whereas species like **3** would have high J_{RhP} coupling constants. For example the carbonyl complex **7** has a high coupling constant, J_{RhP} = 147 Hz.

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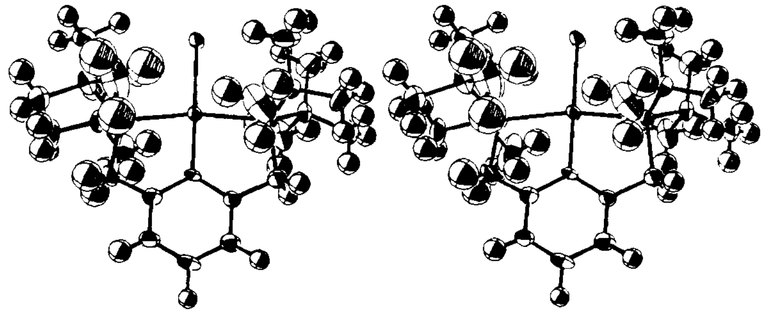

Figure 2. A stereoscopic view of complex 1 with inclusion of hydrogen atoms.

two sets of resonances in the ^{1}H NMR spectrum.

X-ray Structure of [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$]. Figure 1 shows the X-ray molecular structure of 1 and the numbering scheme for the atoms. The structure clearly shows the rhodium atom bonded to the aromatic ring with a Rh–C(5) distance of 1.999 (7) Å. This distance is shorter than the rhodium–carbon distance in [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$], Rh–C = 2.082 (2) Å.[14] The phosphorus atoms are almost trans to each other with a P(2)–Rh–P(3) angle of 168.28 (8)°. The rhodium–phosphorus bond lengths of 2.306 (2) and 2.302 (2) Å are nearly the same; these lengths are comparable to those in the complex [$RhHCl(P(t\text{-}Bu)(n\text{-}Pr)_2)$], 2.31 Å.[15] The Rh–Cl(4) bond distance of 2.425 (2) Å agrees with the corresponding distance of 2.452 (1) Å in the saturated analogue mentioned above. The rhodium atom is displaced 0.043 Å out of the plane which contains P(2), Cl(4), P(3), and C(5). The hydrogen atom bonded to rhodium was not located, although it presumably lies above the rhodium atom.

Experimental Section

All manipulations were performed under pure argon. Nujol mulls were prepared in a Vacuum Atmosphere drybox. The CsI windows were coated with silicone grease around the edges to prevent oxidation of the samples. NMR samples were prepared in the drybox, and the sample tubes were sealed under vacuum. Chemical reactions were performed in Schlenk type glassware with Teflon O-ring joints. No silicone grease was used.

Cyclohexane and pentane were treated with concentrated sulfuric acid until the sulfuric acid layer no longer became yellow. After the solution was washed with water and dried over $CaCl_2$, the pentane was distilled from sodium–benzophenone ketyl and cyclohexane was distilled from $LiAlH_4$. Cyclohexane-d_{12} was treated with D_2SO_4 and purified the same way as described above. Nujol was treated with concentrated sulfuric acid until the acid remained colorless, and then it was washed with water, dried over $CaCl_2$, and distilled under high vacuum over sodium. Benzene was distilled over sodium–benzophenone ketyl, and benzene-d_6 was distilled under vacuum after freeze–thaw degassing from $LiAlH_4$. Hydrogen (99.98% min, Baker), ethylene, (99.5% min, Baker), and CO (99.5% min, Baker) were used without further purification. Trimethylphosphine,[16] methylenetrimethylphosphorane,[16] di-*tert*-butylphosphine,[17] $NaN(SiMe_3)_2$,[18] and 1,3-bis[(*tert*-butylphosphino)methyl]benzene[9] were prepared according to the literature.

Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. Nuclear magnetic resonance spectra were obtained on Varian T-60 and Varian CFT-20 spectrometers for ^{1}H (80 MHz) and ^{13}C (20 MHz). Additional spectra were obtained with a Varian XL-100, ^{1}H (100.1 MHz) and ^{31}P (40.5 MHz), and a Bruker 500-MHz instruments, ^{1}H (500 MHz), ^{31}P (202.47 MHz), ^{2}H (76.77 MHz), and ^{13}C (125.76 MHz). ^{31}P NMR chemical shifts are reported in parts per million relative to external 85% H_3PO_4; downfield shifts are positive. ^{13}C NMR chemical shifts are reported with Me_4Si as an external standard; downfield resonances are positive. ^{1}H and ^{2}H chemical shifts are reported relative to an internal standard of hydrogen atoms in benzene-d_6 (7.15 ppm relative to Me_4Si); downfield resonances are positive.[19]

Preparation of [$ClRhH\{P(t\text{-}Bu_2)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$], 1. A slight modification of Shaw's procedure was used. The bis(phosphine) (1.55 g, 393 mmol) and $RhCl_3 \cdot 3H_2O$ (0.695 g, 2.62 mmol) were allowed to stir at room temperature in 20 mL of isopropyl alcohol and 1 mL of water for 12 h. Then the red-brown mixture was refluxed for 24 hrs whereupon it became orange. The hot solution was filtered and the filtrate cooled to 0 °C to give yellow-orange needles: 0.486 g, 70%; ^{1}H NMR (C_6D_6) δ 1.01, 1.1 (2t, 36, $^3J_{PH} + {}^5J_{PH} = 6.5$ Hz, $C(CH_3)_3$), 2.70, 2.90 (2dt, 4, $PCH_2C_6H_3$, $J_{RhH} = 17.6$ Hz, $J_{PH} = 3.8$ Hz), −27.2, −27.8 (2dt, 1, RhH, $J_{RhH} = 50.8$ Hz, $^2J_{PH} = 12.0$ Hz). These different peaks probably arise from different magnetic environments of the *tert*-butyl methylene and hydride atoms. Compound 1 appears to be photochromic. When a sealed sample is exposed to intense light, the yellow solid becomes red-orange. Shaking this solid in the absence of light causes reversal to the yellow form.

Interaction of [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$] with $NaN(SiMe_3)_2$. A solution of 1 (0.025 g, 0.047 mmol) in pentane was treated portionwise with $NaN(SiMe_3)_2$ (0.009 g, 0.053 mmol). After various time periods, the mixture was filtered and the solvent removed to give a yellow-brown solid: 0.015 g, 65%; IR (Nujol) ν(RhH) 2136 and 1940 cm^{-1}; ^{1}H NMR (C_6D_6) δ −27.5 (dt, 1, RhH, $J_{RhH} = 50.8$ Hz, $^2J_{PH} = 12.0$ Hz); ^{2}H NMR (C_6D_6) δ −27.5 (br, RhD); ^{31}P{^{1}H} NMR (C_6D_6) δ 81.4 (d, $J_{RhP} = 167$ Hz, major),[20] 75.2 (d, $J_{RhP} = 115$ Hz), 73.5 (d, $J_{RhP} = 115$ Hz), 93.0 (dd, $J_{RhP} = 110$ Hz, $^2J_{PP} = 396$ Hz), 72.0 (dd, $J_{RhP} = 110$ Hz, $^2J_{PP} = 396$ Hz).[21]

Interaction of [$ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}$] with $NaN(SiMe_3)_2$ in the Presence of Ethylene Gas. Under 1 atm of C_2H_4, $NaN(SiMe_3)_2$ (0.019 g, 0.1 mmol) was added portionwise to a solution of 1 (0.05 g, 0.09 mmol) in pentane. The yellow solution became red-orange, and the product was isolated after filtration and removal of pentane at −30 °C in vacuo to give a red-orange solid: 0.0296 g, 60%; mp 170–180 °C dec; ^{1}H NMR (C_6D_6) δ 1.2 (36 H, t, $J_{PH} = 6.0$ Hz, $C(CH_3)_3$), 3.2 (4 H, t, $J_{PH} = 2.5$ Hz, CH_2), 4.0 (4 H, br, C_2H_4), 7.1–7.25 (3 H, m, C_6H_3); ^{31}P{^{1}H} NMR (C_6D_6) δ 73.5 (d, $J_{RhP} = 152$ Hz, major),[11] 81.6 (d, $J_{RhP} =$

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152 Hz), 92.4 (d, J_{RhP} = 152 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 31.4 (s, $C(CH_3)_3$), 35.5 (t, J_{PC} = 11.4 Hz, $C(CH_3)_3$), 39.0 (m, CH_2P), 55.0 (br, C_2H_4), 128 (m, C_6H_3).

Interaction of $[ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ with $NaN(SiMe_3)_2$ in the Presence of Carbon Monoxide. A solution of 1 (0.05 g, 0.09 mmol) in pentane was treated portionwise with $NaN(SiMe_3)_2$ (0.019 g, 0.1 mmol) under 1 atm of carbon monoxide. The yellow air-stable product was obtained after filtration and solvent removal in vacuo: yield 0.045 g, 90%; mp 200–210 °C.[9]

Interaction of $[ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ with $NaN(SiMe_3)_2$ or KH in the Presence of Hydrogen Gas. A solution of 1 (0.025 g, 0.047 mmol) in pentane was treated portionwise with $NaN(SiMe_3)_2$ under 1 atm of H_2 gas. After 3 h, the yellow solution was filtered and the pentane removed in vacuo to give an extremely air-sensitive yellow solid: yield 0.015 g, 65%; mp 180–190 °C dec; ^1H NMR (C_6D_6) δ 1.2 (t, 36, J_{PH} = 6.8 Hz, $C(CH_3)_3$), 3.26 (t, 4, J_{PH} = 3.7 Hz, CH_2), 7.1–7.25 (m, 3, C_6H_3), –4.5 (d, 2, J_{RhH} = 16.8 Hz, RhH_2);[22] $^{31}P\{^1H\}$ NMR (C_6D_6) δ 93.5 (d, J_{RhP} = 150 Hz), 81.7 (d, J_{RhP} = 166 Hz), 74.9 (d, J_{RhP} = 117 Hz); $^{31}P\{^1H\}$ NMR (C_6D_{12}) δ 99.0 (d, J_{RhP} = 150 Hz), 87.5 (d, J_{RhP} = 166 Hz), 80.0 (d, J_{RhP} = 110 Hz); $^{13}C\{^1H\}$ NMR (C_6D_{12}) δ 30.4 (t, $^2J_{PC} + {^4J_{PC}}$ = 3.6 Hz, $(CH_3)_3$), 34.5 (t, $^1J_{PC} + {^3J_{PC}}$ = 6.7 Hz, $C(CH_3)_3$), 37.2 (dt, $^1J_{PC} + {^3J_{PC}}$ = 9.5 Hz, $^2J_{RhC}$ = 3.9 Hz, CH_2P), 120.8 (t, $^2J_{PC} + {^4J_{PC}}$ = 9.6 Hz, Ph C-2,6), 122.5 (t, $^2J_{PC} + {^5J_{PC}}$ = 9.4 Hz, Ph C-3,5), 124.0 (s, Ph C-4), 153.0 (dt, $^2J_{PC}$ = 12.9 Hz, J_{RhC} = 3.4 Hz, Ph C-1); IR (Nujol) 2130, 1940, 1890 cm^{-1} (ν(RhH)).

Interaction of $[ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$ with $^-CH_2–PMe_3^+$. A solution of 1 (0.050 g, 0.0925 mmol) in 15 mL of pentane was treated with a solution of $^-CH_2–PMe_3^+$ (0.0084 g, 0.0925 mmol) in 5 mL of pentane at room temperature. A yellow precipitate formed immediately. After 3 h the mixture was filtered and the yellow air-sensitive solid isolated: 0.046 g, 80%; IR (Nujol), 2136, 1940 cm^{-1} (ν(RhH)); ^1H NMR (C_6D_6) δ −11.65, −11.31 (2dt, 1, J_{RhH} = 20 Hz, $^2J_{PH}$ = 5.5 Hz, RhH), 0.45, 0.61 (2d, 9, J_{PH} = 12.5 Hz, $P(CH_3)_3$), 0.68, 0.84 (2dt, 2, $^2J_{PH}$ = 28.6 Hz, $^3J_{PH}$ = 5.5 Hz, $CH_2P(CH_3)_3$) (J_{RhH} not observed), 0.88, 0.99 (2t, 36, $^3J_{PH}$ = 5.5 Hz, $C(CH_3)_3$), 2.89, 2.77 (2t, 4, $^2J_{PH}$ = 3.7 Hz, $C_6H_3CH_2P$), 6.37–6.80 (2t, 1, J_{HH} = 6.9 Hz, p-H) 6.61, 6.92 (2d, 2, J_{HH} = 7.4 Hz, m-H); $^{31}P\ \{^1H\}$ NMR (THF-d_8) δ 72.0 (d, $^1J_{RhP}$ = 170 Hz, P–Rh), 79.0 (d, $^1J_{RhP}$ = 170 Hz, P–Rh), 24.2 (d, $^2J_{RhP}$ = 25.0 Hz, CH_2PMe_3), 33.0 (d, $^2J_{RhP}$ = 25.0 Hz, CH_2PMe_3); $^{13}C\{^1H\}$ NMR (THF-d_8) δ 31.5, 30.3 (2s, $(CH_3)_3$), 35.3, 35.9 (2d, J_{PC} = 7.8 Hz, $C(CH_3)_3$), 36.6, 40.4 (2t, $^1J_{PC} + {^3J_{PC}}$ = 16.5 Hz, $C_6H_3CH_2P$), 151.1 (dt, $^2J_{PC}$ = 12.4 Hz, J_{RhC} = 3.8 Hz, Ph C-1), 118.8 (t, $^2J_{PC}$ = 7.6 Hz, Ph C-2,6), 118.5 (s, Ph C-3,5), 118.9 (s, Ph C-4), 0.8, −18.0 (2dtd, $^1J_{PC}$ = 46.0 Hz, $^2J_{PC}$ = 12.4 Hz, $^1J_{RhC}$ = 3.8 Hz, $RhCH_2PMe_3$), 18.5, 25.9 (d, $^1J_{PC}$ = 51.0 Hz, $P(CH_3)_3$).

Preparation of *tert*-Butyl-d_9 Chloride. A solution of CD_3I (34 g, 0.234 mol) in 30 mL of ether was added to 5.7 g (0.234 mol) of Mg turnings in 30 mL of ether in a 300 mL flask equipped with a reflux condenser and mechanical stirrer. The ether solution was added over an 80-min period in order to maintain gentle reflux. After 30 additional minutes of reflux, the mixture was ice cooled, and 15.02 g (0.234 mol) of acetone-d_6 in 18 mL of ether was added dropwise; leftover Mg was not filtered from the mixture. The mixture was stirred overnight and hydrolyzed by adding 120–130 mL of ice-cold water, followed by 45 mL of 30% acetic acid.

The ether was distilled and the alcohol–water azeotrope was collected at 60–96 °C. This mixture was treated with five times the volume of concentrated HCl in a separatory funnel. The *tert*-butyl-d_9 chloride which formed immediately was separated from the water layer and dried over $CaCl_2$. The product was collected at 48–52 °C (14 mL, 12.2 g, 52%).

Table I. Crystallographic Data and Data Collection Parameters for $[ClRhH\{P(t\text{-}Bu)_2CH_2C_6H_3CH_2P(t\text{-}Bu)_2\}]$

formula	$RhC_{24}H_{44}P_2Cl$
fw	532.92
cryst system	orthorhombic
space group	$Pc2_1n$ (standard setting $Pna2_1$)
a, Å	7.879 (3)
b, Å	14.388 (4)
c, Å	22.868 (5)
V, Å^3	2592.4 (12)
Z	4
ρ(calcd), g cm^{-3}	1.36
ρ(obsd), g cm^{-3}	1.32
μ, cm^{-1}	8.821
diffractometer	Syntex $P\bar{1}$
temp, K	115
radiatn	Mo Kα (λ = 0.710 69 Å)
monochromator	graphite
scan mode	θ-2θ
scan speed, deg min^{-1}	6.0
2θ range, deg	$2 < 2\theta < 50$
reflctns measd	$+h,+k,+l$
unique reflctns collectd	2400
reflctns used in refinement with $I > 3\sigma(I)$	2152
R and R_w[25]	0.040 and 0.052
goodness of fit[25]	1.75

X-ray Data Collection and Structure Determination. Crystal data and pertinent details of data collection and refinement are given in Table I.

A golden crystal of approximate dimensions 0.15 × 0.22 × 0.30 mm, grown by slow crystallization from isopropyl alcohol, was mounted on a Syntex $P\bar{1}$ automatic diffractometer equipped with a low-temperature device.[23] Automatic centering of 15 independent reflections indicated an orthorhombic system with cell parameters listed in Table I, and systematic absences suggested the space groups $Pcmm$ and $Pc2_1n$ (alternate standard settings of $Pnma$ and $Pna2_1$ respectively). Procedures for data collection have been described previously.[24] Three check reflections monitored after every 97 reflections showed no appreciable decay in intensity. The data were corrected for Lorentz and polarization effects and for the absorption of X-rays.

Intensity statistics strongly indicated the space group to be noncentrosymmetric; hence, the space group $Pc2_1n$ was assumed and subsequently confirmed by the successful solution and refinement of the structure. The positional coordinates of a Rh and a P atom were obtained by a combination of Patterson and direct methods. A difference Fourier map phased on the refined coordinates of the Rh and P atoms revealed the positions of all the non-hydrogen atoms in the asymmetric unit. Full-matrix least-squares refinement with isotropic thermal parameters for all non-hydrogen atoms converged with R = 0.149.[25] Further anisotropic refinement of all non-hydrogen atoms reduced the R value to 0.051. Positions of the ring hydrogen atoms and of at least one hydrogen atom attached to each methyl carbon of the *tert*-butyl moiety were determined from difference Fourier syntheses while positions of the remaining hydrogen atoms were calculated by assuming idealized geometries. The hydride ligand was not located. The hydrogen atoms were assigned an isotropic thermal parameter equivalent to that of the carbon atom to which it was bonded. Full-matrix least-squares refinement with anisotropic thermal parameters for the non-hydrogen atoms and with the hydrogen atom parameters fixed converged at R = 0.040 and R_w = 0.052.[25] A final difference map revealed no additional

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(22) $^1H\{^{31}P\}$ decoupling experiments showed that the doublet at δ −4.5 was unchanged. $^1H\{^{103}Rh\}$ decoupling experiments showed a broad singlet at δ −4.5 with unresolved $^2J_{PH}$. The $^{103}Rh\{^1H\}$ resonance showed a triplet at δ −995 ± (J_{RhP} = 167 Hz). We thank Prof. B. Heaton, University of Kent, Canterbury, and Prof. R. Goodfellow University of Bristol for these experiments.

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(25) $R = (\sum||F_o| - |F_c||)/(\sum|F_o|)$ and $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ where F_o and F_c are the observed and calculated structure factors, respectively, and $w = 1/\sigma^2(F_o)$. The parameter minimized in all least-squares refinements is $\sum w(|F_o| - |F_c|)^2$. The goodness of fit (GOF) is given by GOF = $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO is the number of observations and NV is the number of variables.

Table II. Final Positional and Thermal Parameters[a] ($\times 10^3$) with Esd's for [ClRhH{P(*t*-Bu)$_2$CH$_2$C$_6$H$_3$CH$_2$P(*t*-Bu)$_2$}]

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Rh	0.1584 (1)	0.8425 (0)	0.0823 (0)	47 (0)	27 (0)	20 (0)	19 (0)	4 (0)	3 (0)
P(2)	0.0712 (3)	0.8714 (1)	0.1768 (1)	34 (1)	22 (1)	20 (1)	7 (1)	2 (1)	1 (1)
P(3)	0.2677 (4)	0.7876 (2)	−0.0044 (1)	64 (2)	61 (2)	21 (1)	43 (1)	2 (1)	−2 (1)
Cl(4)	0.0019 (3)	0.9695 (2)	0.0381 (1)	68 (1)	35 (1)	24 (1)	34 (1)	13 (1)	13 (1)
C(5)	0.2764 (11)	0.7334 (5)	0.1180 (3)	37 (5)	26 (4)	29 (4)	21 (4)	−6 (4)	−1 (3)
C(6)	0.2775 (11)	0.7175 (6)	0.1791 (4)	33 (5)	24 (4)	29 (4)	5 (3)	2 (4)	5 (3)
C(7)	0.3521 (11)	0.6394 (7)	0.2032 (4)	30 (5)	43 (5)	40 (5)	6 (4)	7 (4)	12 (4)
C(8)	0.4255 (11)	0.5731 (6)	0.1667 (4)	36 (5)	23 (4)	55 (6)	12 (4)	−1 (4)	8 (4)
C(9)	0.4324 (12)	0.5890 (7)	0.1066 (4)	51 (6)	42 (5)	47 (5)	21 (5)	−23 (5)	−15 (4)
C(10)	0.3612 (14)	0.6685 (8)	0.0836 (4)	76 (7)	46 (6)	36 (5)	36 (5)	−12 (5)	−5 (4)
C(11)	0.3848 (26)	0.6841 (12)	0.0192 (5)	271 (21)	156 (16)	31 (6)	194 (17)	−9 (9)	−11 (7)
C(12)	0.2001 (11)	0.7896 (6)	0.2193 (4)	47 (5)	35 (5)	33 (4)	10 (4)	4 (4)	7 (4)
C(13)	−0.1551 (10)	0.8355 (8)	0.1893 (3)	36 (4)	36 (4)	30 (3)	−2 (4)	1 (3)	1 (5)
C(14)	−0.2126 (11)	0.8332 (11)	0.2526 (3)	42 (5)	110 (9)	27 (4)	−17 (7)	0 (4)	16 (6)
C(15)	−0.2743 (12)	0.8962 (9)	0.1547 (5)	31 (5)	90 (9)	65 (6)	10 (5)	−2 (5)	33 (6)
C(16)	−0.1617 (16)	0.7355 (9)	0.1637 (7)	65 (8)	56 (7)	134 (13)	−29 (6)	16 (8)	−39 (8)
C(17)	0.1193 (11)	0.9872 (6)	0.2111 (3)	37 (5)	33 (5)	27 (4)	−4 (4)	4 (3)	−8 (4)
C(18)	0.3055 (16)	1.0121 (10)	0.1939 (6)	58 (7)	75 (9)	66 (8)	−12 (7)	16 (6)	−23 (7)
C(19)	0.1133 (13)	0.9867 (7)	0.2777 (4)	55 (6)	53 (6)	37 (5)	4 (5)	−1 (4)	−20 (5)
C(20)	0.0016 (18)	1.0621 (6)	0.1876 (5)	114 (10)	19 (4)	62 (6)	15 (6)	−14 (7)	−10 (4)
C(21)	0.1036 (12)	0.7424 (7)	−0.0568 (4)	48 (8)	35 (5)	48 (5)	1 (4)	14 (5)	−8 (4)
C(22)	0.0225 (12)	0.8222 (7)	−0.0911 (5)	47 (5)	47 (7)	70 (7)	11 (5)	−24 (5)	−22 (5)
C(23)	0.1673 (16)	0.6680 (9)	−0.1015 (5)	93 (9)	59 (7)	55 (6)	24 (7)	−11 (6)	−17 (6)
C(24)	−0.0347 (23)	0.6964 (10)	−0.0172 (8)	156 (15)	62 (8)	132 (13)	−44 (10)	85 (12)	−26 (9)
C(25)	0.4323 (10)	0.8658 (10)	−0.0429 (4)	20 (4)	140 (13)	40 (5)	17 (6)	−6 (4)	−36 (7)
C(26)	0.5134 (14)	0.8128 (10)	−0.0941 (4)	51 (6)	124 (13)	40 (5)	9 (7)	8 (4)	−33 (6)
C(27)	0.3532 (16)	0.9563 (11)	−0.0609 (6)	89 (10)	85 (10)	84 (9)	−27 (8)	59 (8)	−31 (8)
C(28)	0.5715 (16)	0.8886 (19)	0.0017 (6)	50 (7)	330 (34)	79 (9)	−9 (13)	−8 (7)	−81 (15)

[a] The complete temperature factor is $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Selected Bond Distances (Å) and Angles (deg)

		Distances			
Rh-Cl(4)	2.425 (2)	C(5)-C(6)	1.416 (11)	C(17)-C(18)	1.560 (14)
Rh-P(2)	2.306 (2)	C(6)-C(7)	1.383 (12)	C(17)-C(19)	1.523 (12)
Rh-P(3)	2.302 (2)	C(7)-C(8)	1.393 (13)	C(17)-C(20)	1.520 (13)
Rh-C(5)	1.999 (7)	C(8)-C(9)	1.394 (14)	C(21)-C(24)	1.564 (16)
P(2)-C(12)	1.833 (8)	C(9)-C(10)	1.378 (13)	C(21)-C(22)	1.530 (14)
P(2)-C(13)	1.878 (8)	C(10)-C(11)	1.501 (15)	C(21)-C(23)	1.563 (14)
P(2)-C(17)	1.880 (8)	C(6)-C(12)	1.515 (11)	C(25)-C(26)	1.536 (13)
P(3)-C(11)	1.833 (11)	C(13)-C(14)	1.518 (10)	C(25)-C(27)	1.501 (20)
P(3)-C(21)	1.879 (10)	C(13)-C(15)	1.508 (13)	C(25)-C(28)	1.532 (15)
P(3)-C(25)	1.929 (12)	C(13)-C(16)	1.554 (16)		
		Angles			
P(2)-Rh-Cl(4)	95.90 (7)	Rh-P(3)-C(21)	114.3 (3)	P(3)-C(21)-C(24)	104.9 (9)
P(2)-Rh-C(5)	84.11 (22)	Rh-P(3)-C(25)	116.4 (3)	P(3)-C(25)-C(26)	109.7 (9)
P(3)-Rh-Cl(4)	95.16 (7)	P(2)-C(12)-C(6)	109.9 (6)	P(3)-C(25)-C(27)	110.6 (6)
P(3)-Rh-C(5)	84.75 (23)	P(2)-C(13)-C(14)	115.7 (6)	P(3)-C(25)-C(28)	107.6 (10)
P(2)-Rh-P(3)	168.82 (8)	P(2)-C(13)-C(15)	110.6 (7)	C(5)-C(10)-C(11)	120.9 (9)
C(5)-Rh-Cl(4)	176.89 (26)	P(2)-C(13)-C(16)	103.3 (7)	C(5)-C(6)-C(12)	119.1 (7)
Rh-C(5)-C(6)	122.2 (6)	P(2)-C(17)-C(18)	106.7 (6)	C(5)-C(6)-C(7)	121.8 (8)
Rh-C(5)-C(10)	121.3 (6)	P(2)-C(17)-C(19)	113.9 (6)	C(6)-C(7)-C(8)	119.7 (8)
Rh-P(2)-C(12)	102.5 (3)	P(2)-C(17)-C(20)	111.0 (6)	C(7)-C(8)-C(9)	119.6 (8)
Rh-P(2)-C(13)	112.1 (2)	P(3)-C(11)-C(10)	110.4 (7)	C(8)-C(9)-C(10)	119.8 (8)
Rh-P(2)-C(17)	119.4 (3)	P(3)-C(21)-C(22)	110.7 (6)	C(9)-C(10)-C(5)	122.4 (8)
Rh-P(3)-C(11)	102.3 (4)	P(3)-C(21)-C(23)	115.7 (7)	C(6)-C(5)-C(10)	116.5 (7)

chemical features in the structure. The largest peak in the map, 1.7 e/Å^3 in height, is within 1 Å from the coordinated chlorine atom.

All calculations were performed on a DEC VAX 11/780 departmental computer at UCLA. The programs used in this work included modified versions of the following: DATRED (Bell and Murphy), MULTAN (Main), ORFLS (Busing, Martin, and Levy), ORFFE (Busing, Martin, and Levy), ABSORB (Coppens, Edwards, and Hamilton), and ORTEP (Johnson). For the structure factor calculations, neutral atom scattering factors were used and corrections for anomalous dispersion were applied.[26]

Final positional and thermal parameters of the non-hydrogen atoms are given in Table II. Selected interatomic distances and angles with their estimated standard deviations are presented in Table III. Tables of hydrogen atom parameters (Table IV), least-squares planes, interplanar angles, and atomic deviations from these planes (Table V), selected torsion angels (Table VI), and observed and calculated structure factor amplitudes (Table VII) have been deposited. An ORTEP drawing of the molecular structure with the atom labeling scheme and a stereoview of the molecule with the hydrogen atoms included are shown in Figures 1 and 2, respectively.

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[26] Cromer, D. T.; Waber, J. T. "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2A and 2.3.1.

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Supplementary Material Available: Listings of final positional and thermal parameters for the hydrogen atoms, least-squares planes, selected interplanar angles and atomic deviations, selected torsion angles, and observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

Pyrazolyl-Bridged Iridium Dimers.[1] 4. Crystal and Molecular Structures of Bis(cycloocta-1,5-diene)bis(μ-pyrazolyl)diiridium(I), Its Dirhodium(I) Isomorph, and Two Bis(cycloocta-1,5-diene)diiridium(I) Analogues Incorporating 3,5-Disubstituted μ-Pyrazolyl Ligands

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The crystal and molecular structures of the homobimetallic complexes $[M(COD)(\mu\text{-pz})]_2$ (1, M = Ir, 2, M = Rh; COD = cycloocta-1,5-diene, pzH = pyrazole), $[Ir(COD)(\mu\text{-fpz})]_2$ (3, fpzH = 3,5-bis(trifluoromethyl)pyrazole], and $[Ir(COD)(\mu\text{-}3\text{-}CH_3,5\text{-}CF_3C_3N_2H)]_2$ (4, derived from 3-methyl-5-(trifluoromethyl)pyrazole) have been determined by single-crystal X-ray diffraction. Compounds 1 and 2 are isomorphous, crystallizing in the space group *Cmcm* with a = 12.750 (4) Å, b = 12.037 (4) Å, and c = 13.432 (4) Å and a = 12.745 (4) Å, b = 12.019 (4) Å, and c = 13.405 (4) Å, respectively: the two molecules are virtually identical with Ir–Ir = 3.216 (1) Å in 1 and Rh–Rh = 3.267 (2) Å in 2, indicating that observed differences in reactivity originate from electronic effects. Compound 3, space group $P\bar{1}$ with a = 11.604 (5) Å, b = 11.968 (5) Å, c = 11.131 (4) Å, α = 95.10 (4)°, β = 97.52 (4)°, and γ = 110.32 (3)°, is sterically crowded by the substituent CF_3 groups in the μ-fpz unit in a way which accords with the remarkably inert character of this complex compared with 1 and which may also be responsible for the significant contraction in Ir–Ir, to 3.073 (1) Å. The structure of compound 4 is disordered in terms of CH_3,CF_3 site occupancy, but in this molecule also Ir–Ir is short at 3.066 (2) Å.

We recently described[2] the synthesis and some properties of the diiridium(I) complex $[Ir(COD)(\mu\text{-pz})]_2$ (1, COD = cycloocta-1,5-diene, pzH = pyrazole). The rhodium analogue 2 of compound 1 was first reported in 1971 by Trofimenko.[3] We have demonstrated an unusual structure for 1, wherein despite being linked through two atoms in the heterocyclic bridge the d^8 Ir centers are brought to close proximity (3.216 Å) and have uncovered an extensive chemistry a salient feature of which is[2] oxidative addition by a variety of substrates to give diiridium(II) products without fragmentation of the dimeric unit (eq 1). We have

$$[Ir(COD)(\mu\text{-pz})]_2 + XY = [(COD)Ir(X)(\mu\text{-pz})_2Ir(COD)(Y)] \quad (1)$$

also established that parallel reactivity is not a property of compound 2 for which we find no evidence for formation of isolable adducts with, for example, MeI or activated acetylenes. Complexes 1 and 2 do resemble each other, however, in that on treatment with CO, COD is displaced from either one to give an unstable tetracarbonyl dimer, which will react further with PPh_3 affording the carbonyl phosphine analogues $[M(CO)(PPh_3)(\mu\text{-pz})]_2$ (M = Rh or Ir). Each of the latter will undergo two-center oxidative addition, the Ir_2 species being the more reactive, inter alia slowly forming a dihydrogen adduct and yielding cationic complexes with HPF_6. In this context we have already reported[4] an X-ray study of $[Ir(CO)(PPh_3)(\mu\text{-pz})]_2$ and its

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