parameters for the crystal structure are presented in Table I and in Table S1 of the supplementary material (see the paragraph at the end of the paper). The intensity data for structure of 3 showed no evidence of decay upon X-ray irradiation. The structure was solved by standard heavy-atom methods with all remaining non-hydrogen atoms located through a succession of difference Fourier maps and least-squares refinements. In the final refinement model, all non-hydrogen atoms were refined anisotropically with hydrogen atoms placed at calculated positions. Table II contains the final refined positional and isotropic thermal parameters for the structure. The supplementary material contains the final anisotropic thermal parameters, the calculated hydrogen positional parameters, complete tabulations of bond distances and angles, and a listing of observed and calculated structure factor amplitudes for the structure.

Acknowledgment. We thank the National Science Foundation (CHE 86-03055 and 89-09060) for support of this work and the Johnson Matthey Co., Inc. for a generous loan of iridium trichloride. P.P.D. gratefully acknowledges Sherman Clarke and Elon Huntington Hooker Fellowships.

Supplementary Material Available: Tables of data collection and refinement parameters, final positional parameters, calculated hydrogen positional parameters, complete bond distances and angles, and anisotropic thermal parameters (11 pages); a listing of observed and calculated structure factors (22 pages). Ordering information is given on any current masthead page.

Catalytic Functionalization of C–H Bonds by Isonitrile Insertion. Preparation, Characterization, and Reactivity of $RhCl(PR_3)_2(CNR')$

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A series of complexes of the type *trans*-$RhCl(PR_3)_2(CNR')$, where R = Me, Et, *i*-Pr and R′ = neopentyl, 2,6-xylyl, or Me, have been prepared and examined for C–H bond activation. All of the neopentyl complexes produce 2,2-dimethyl-5-phenyl-4-aza-4-pentene (**5a**) upon irradiation in benzene solvent. In the presence of low concentrations of added isonitrile the production of **5a** is catalytic, with the R = isopropyl giving the highest yields. Two of the precursors were structurally characterized. The *trans*-$RhCl[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)$ (**2c**) crystallizes in the monoclinic space group $P2_1/c$ with $a = 13.894$ (5) Å, $b = 12.014$ (6) Å, $c = 18.896$ (9) Å, $\beta = 103.58$ (4)°, $V = 3066$ (5) Å^3, and $Z = 4$. The complex *trans*-$RhCl[P(i\text{-}Pr)_3]_2(CN\text{-}2,6\text{-xylyl})$ (**2e**) crystallizes in orthorhombic space group *Pnna* with $a = 14.620$ (2) Å, $b = 16.07$ (2) Å, $c = 15.358$ (4) Å, $V = 3608$ (5) Å^3, and $Z = 4$. At higher concentrations, a solution of **2c** and neopentyl isocyanide in benzene produces the complex $\{trans\text{-}Rh[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)_2\}^+Cl^-$ (**3a**), which precipitates from solution. Complex **3a** crystallizes in the monoclinic space group $P2_1/n$ with $a = 11.633$ (3) Å, $b = 13.945$ (3) Å, $c = 23.050$ (9) Å, $\beta = 92.69$ (2)°, $V = 3735$ (3) Å^3, and $Z = 4$. Complex **3a** is also found to serve as a catalyst for production of **5a**, but the PF_6^- salt **3b** is inactive.

Introduction

Saturated hydrocarbons are an abundant and inexpensive source of reduced carbon that would be suitable for use in the synthesis of organic compounds if it were not for their low reactivity. Methods presently used in industry for the functionalization of saturated hydrocarbons are typically inefficient, giving either a poor conversion of alkane or a lack of regioselectivity resulting in product mixtures.[1] The recent reports of the intermolecular activation of C–H bonds in alkanes by homogeneous transition-metal complexes, now becoming common in the chemical literature,[2] indicate that this reaction can be induced under mild thermal or photochemical homogeneous conditions with high regioselectivity.[3]

In spite of the recent increase in understanding the kinetics, thermodynamics, and mechanism(s) of this reaction,[4] the practical application of homogeneous C–H activation toward the development of a low-energy and selective alternative to the presently used industrial processes for the functionalization of saturated hydrocarbons remains a challenge for researchers. However, many significant advances have been recently achieved, most notably in the areas of alkane dehydrogenation[5,7] and carbonylation.[6,8] Both catalytic cycles suffer in that the overall reaction is thermodynamically unfavorable. In

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† A. P. Sloan Fellow, 1984–86. Camille & Henry Dreyfus Teacher Scholar, 1985–89.

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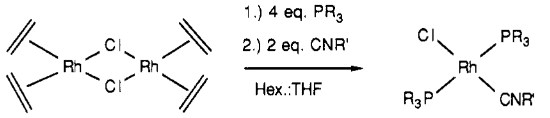
most instances the dehydrogenation requires the presence of a hydrogen acceptor,[8] but reports of catalytic dehydrogenation in the absence of hydrogen acceptors have appeared in which high-intensity UV irradiation provides the driving force for the process.[7]

Two examples of the catalytic carbonylation of saturated hydrocarbons (presumed to be photochemically driven) have been reported.[6] The catalytic carbonylation of unsaturated hydrocarbons has also been successful,[8] although it has been shown that the reverse reaction (catalytic decarbonylation) is thermodynamically favorable.[8]

Recently, work in our laboratory has led to the first report of hydrocarbon functionalization via catalytic isonitrile insertion into the C–H bonds of benzene using $Fe(PMe_3)_2(CNR)_3$ as the catalyst.[9] Unlike the isoelectronic alkane carbonylation process described above, the overall reaction in this case is thermodynamically favorable ($\Delta G \simeq -5$ kcal/mol). Unfortunately the $Fe(PMe_3)_2(CNR)_3$ system does not functionalize saturated hydrocarbons. A related series of experiments showed that $Ru(dmpe)_2H_2$ was capable of activating and functionalizing sp^3-hybridized C–H bonds to catalytically produce indoles from aromatic isonitriles.[10] In light of the success by Tanaka in the carbonylation of alkanes using the square-planar complex $RhCl(CO)(PMe_3)_2$ as a catalyst,[6] combined with our research with isonitriles, we proposed that the isonitrile complexes $RhCl(PR_3)_2(CNR')$ might be capable of functionalizing arenes and alkanes via isonitrile insertion. This report describes the synthesis, structural characterization, and reaction chemistry of the new class of square-planar rhodium(I) complexes of the type *trans*-$RhCl(PR_3)_2(CNR')$, including the isonitrile insertion studies in which these complexes were used as catalysts.

Results and Discussion

Synthesis of $RhCl(PR_3)_2(CNR')$, 2a–f. The syntheses of compounds **2a–f** are all similar and involve the "one pot" reaction of di-μ-chlorotetrakis(ethylene)dirhodium(I) (**1**) with 4 equiv of the appropriate trialkylphosphine and 2 equiv of the desired isonitrile in a hexane:THF solvent mixture (eq 1). Both the phosphine and the isonitrile are added slowly to the rhodium dimer in dilute hexane solution in order to avoid the irreversible formation of insoluble rhodium(I) salts.[11] These rhodium salts (known to be of type **3**,[12] vide infra), resulting from the associative displacement of chloride ion from the coordination sphere of rhodium, are the major products isolated in reactions conducted in more polar solvents (neat THF or CH_2Cl_2) or in reactions where the ligands must be added all at once to a stirred solution of **1** due to their method of handling (e.g., the synthesis of **2a,d,f**). But even in cases where appreciable amounts of rhodium(I) salts are formed, the desired product is easily separated from the salts by extraction of the crude product into benzene solution. The crude products isolated in this fashion are usually spectroscopically pure. Due to large differences in the solubility and air stability of each complex, the final purification procedure for obtaining analytically pure samples varies.

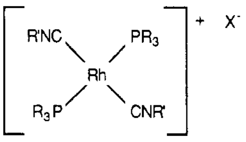


(1)

1 **2**

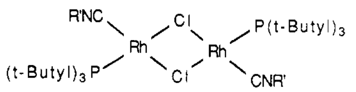
2	R	R'
a	methyl	neopentyl
b	ethyl	neopentyl
c	*i*-propyl	neopentyl
d	methyl	2,6-xylyl
e	*i*-propyl	2,6-xylyl
f	methyl	methyl

Although it initially appeared that the experimental procedure was a general method for the preparation of complexes of type **2**, there appear to be certain limitations. The reaction of **1** with tri-*tert*-butylphosphine (a sterically bulky ligand) and neopentylisonitrile resulted in the formation of a complex product mixture that when dissolved in a minimum of hexane and cooled to −20 °C for 5 days, yielded a small amount of dark red crystals. The red product is tentatively assigned as that of the chlorine-bridged rhodium dimer **4** (approximately 8% yield) on the basis of its ^1H NMR, ^{31}P NMR, and IR spectra.



3

3	X
a	Cl^-
b	PF_6^-



4

All attempts to synthesize the 1,2-bis(dimethylphosphino)ethane (DMPE) derivative (a *cis*-diphosphine adduct) were also unsuccessful and resulted in the formation of intractable solids (presumably rhodium(I) salts[13]). The substitution of di-μ-chlorobis(1,5-cyclooctadiene)dirhodium(I) for **1** in the preparations resulted in the formation of a complex product mixture from which the desired product could not be isolated in pure form. The chelating cyclooctadiene ligand is more strongly bound to rhodium than ethylene, and phosphine appears to preferentially displace chloride ion in the first step of the reaction.[14]

Characterization of 2a–f. All of the complexes **2a–f** are yellow or yellow–orange solids with the exception of **2b**, which is a yellow liquid. All of the complexes appear to be air stable in the pure state for short periods of time, but prolonged exposure to the atmosphere results in slow decomposition. The air stability of each complex in solution varies dramatically and increases with an increase in the bulk of the alkyl substituent on the phosphine ligand. Consequently, compounds **2a,d,f** are extremely air sensitive in benzene solution while **2b** is moderately air sensitive. Compounds **2c,e** are air stable in benzene solution for extended periods. Complexes **2a–f** have been fully characterized by ^1H NMR, ^{31}P NMR, ^{13}C NMR, IR, UV–vis, and elemental analysis. It was also possible to obtain mass spectral data for complexes **2a,d**.

The solid-state structures for complexes **2c** and **2e** were obtained by single-crystal X-ray diffraction. They both display square-planar structures with trans phosphines, as shown in Figures 1 and 2. The stronger π-acceptor xylyl isocyanide adopts a linear geometry with a slightly longer

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Table I. Positional Parameters and B(eq) Values for $RhCl[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)$

atom	x	y	z	B(eq), Å^2
Rh	0.20532 (2)	−0.18060 (2)	−0.38720 (1)	3.84 (1)
Cl	0.17415 (9)	−0.2697 (1)	−0.50338 (5)	6.28 (5)
P1	0.14182 (7)	−0.33303 (7)	−0.33763 (5)	4.05 (4)
P2	0.28006 (7)	−0.03283 (8)	−0.43261 (6)	4.60 (4)
N	0.2492 (3)	−0.0742 (3)	−0.2399 (2)	6.7 (2)
C1	0.2310 (3)	−0.1144 (3)	−0.2972 (2)	4.9 (2)
C2	0.2489 (4)	−0.0322 (5)	−0.1689 (3)	8.9 (3)
C3	0.3432 (3)	0.0089 (4)	−0.1255 (2)	5.9 (2)
C4	0.3341 (5)	0.0395 (7)	−0.0507 (3)	11.1 (4)
C5	0.4178 (7)	−0.078 (1)	−0.1190 (5)	21.2 (8)
C6	0.380 (1)	0.1017 (8)	−0.1608 (4)	18.9 (7)
C7	0.0845 (4)	−0.2972 (4)	−0.2608 (2)	6.5 (2)
C8	0.0067 (4)	−0.2076 (5)	−0.2819 (3)	8.4 (3)
C9	0.0558 (6)	−0.3870 (5)	−0.2165 (3)	11.0 (4)
C10	0.0513 (3)	−0.4183 (3)	−0.4036 (2)	5.1 (2)
C11	−0.0377 (3)	−0.3511 (5)	−0.4397 (3)	7.3 (2)
C12	0.0224 (4)	−0.5297 (4)	−0.3767 (3)	7.6 (2)
C13	0.2395 (4)	−0.4326 (4)	−0.2977 (3)	7.1 (2)
C14	0.3172 (4)	−0.3779 (5)	−0.2349 (4)	10.7 (3)
C15	0.2881 (5)	−0.4789 (5)	−0.3548 (4)	10.8 (4)
C16	0.2941 (4)	0.0964 (3)	−0.3770 (2)	6.4 (2)
C17	0.3625 (6)	0.1869 (4)	−0.3913 (4)	10.7 (4)
C18	0.1929 (5)	0.1438 (5)	−0.3722 (3)	8.8 (3)
C19	0.4100 (3)	−0.0673 (4)	−0.4321 (3)	6.2 (2)
C20	0.4166 (4)	−0.1606 (4)	−0.4839 (4)	7.9 (3)
C21	0.4672 (3)	−0.0955 (5)	−0.3550 (3)	8.5 (3)
C22	0.2210 (3)	0.0015 (4)	−0.5281 (2)	6.0 (2)
C23	0.2702 (5)	0.0900 (5)	−0.5644 (3)	10.0 (3)
C24	0.1111 (4)	0.0227 (5)	−0.5376 (3)	7.9 (3)

Table II. Positional Parameters and B(eq) Values for $RhCl[P(i\text{-}Pr)_3]_2$(CN-2,6-xylyl)

atom	x	y	z	B(eq), Å^2
Rh	0.13782 (2)	1/4	1/4	2.88 (2)
Cl	−0.02596 (8)	1/4	1/4	4.53 (6)
P	0.13533 (6)	0.23891 (5)	0.40150 (6)	3.15 (4)
N	0.3435 (3)	1/4	1/4	4.4 (2)
C1	0.2630 (3)	1/4	1/4	3.4 (2)
C2	0.4389 (3)	1/4	1/4	3.6 (2)
C3	0.4857 (3)	0.1765 (3)	0.2285 (2)	4.0 (2)
C4	0.5801 (3)	0.1793 (3)	0.2289 (2)	5.4 (2)
C5	0.6258 (4)	1/4	1/4	6.1 (4)
C6	0.4337 (4)	0.0983 (3)	0.2063 (4)	7.0 (3)
C7	0.1080 (3)	0.3397 (2)	0.4566 (3)	4.6 (2)
C8	0.1752 (4)	0.4061 (3)	0.4244 (3)	7.7 (3)
C9	0.0109 (4)	0.3679 (3)	0.4425 (4)	8.4 (3)
C10	0.2462 (3)	0.2094 (3)	0.4524 (3)	4.8 (2)
C11	0.2628 (3)	0.2291 (3)	0.5467 (3)	7.0 (3)
C12	0.2719 (3)	0.1196 (3)	0.4301 (3)	6.3 (2)
C13	0.0466 (2)	0.1661 (2)	0.4408 (3)	4.2 (2)
C14	0.0475 (3)	0.0831 (3)	0.3914 (3)	6.3 (2)
C15	0.0429 (3)	0.1520 (3)	0.5392 (3)	7.0 (3)
C16	0.8128 (4)	0.0598 (3)	0.2326 (5)	8.5 (4)
C17	0.7816 (4)	0.0300 (4)	0.1577 (4)	7.7 (4)
C18	0.7820 (4)	0.0298 (5)	0.3083 (4)	9.5 (5)

Table III. Selected Distances (Å) and Angles (deg) for $RhCl[P(i\text{-}Pr)_3]_2$(CNR) Complexes

dist			angle		
bond	R = CH_2CMe_3	R = 2,6-xylyl	bonds	R = CH_2CMe_3	R = 2,6-xylyl
Rh–P1	2.323 (1)	2.334 (1)	P1–Rh–P2	175.88 (4)	178.21 (5)
Rh–P2	2.321 (2)	2.334 (1)	P1–Rh–Cl	90.76 (5)	89.11 (3)
Rh–Cl	2.389 (2)	2.395 (1)	P1–Rh–Cl	88.7 (1)	90.89 (3)
Rh–C1	1.834 (4)	1.830 (5)	P2–Rh–C6	90.18 (6)	89.11 (3)
C1–N	1.159 (5)	1.177 (6)	P2–Rh–C1	90.2 (1)	90.89 (3)
N–C2	1.434 (6)	1.395 (6)	C6–Rh–C1	178.9 (1)	180.0
			Rh–C1–N	178.4 (4)	180.0
			C1–N–C2	166.8 (4)	180.0

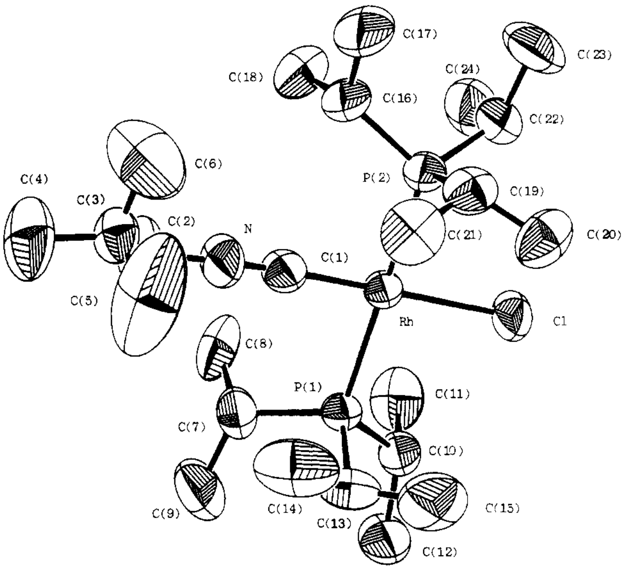


Figure 1. ORTEP diagram of $RhCl[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)$. Ellipsoids are shown at the 50% level.

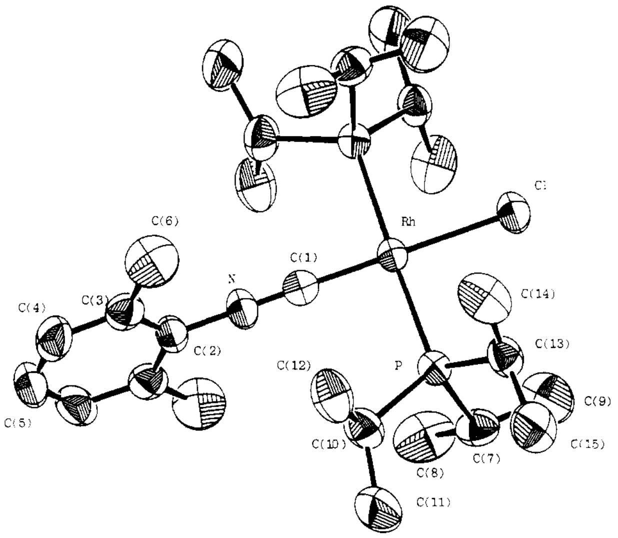


Figure 2. ORTEP diagram of $RhCl[P(i\text{-}Pr)_3]_2$(CN-2,6-xylyl). Ellipsoids are shown at the 50% level.

Table IV. Infrared Spectra for 2a–f

	PR_3	isonitrile	medium	$\nu_{C=N}$, cm^{-1}
2a	Me	neopentyl	C_6H_6	2087 (s), 2031 (w)
2b	Et	neopentyl	C_6H_6	2070 (s), 2031 (w)
2c	*i*-Pr	neopentyl	CH_2Cl_2	2067 (s), 2035 (w), 1986 (w)
			C_6H_{12}	2056 (s), 2032 (s), 1992 (s)
			KBr	2056 (s), 2032 (w)
2d	Me	2,6-xylyl	C_6H_6	2048 (s), 2014 (s)
2e	*i*-Pr	2,6-xylyl	CH_2Cl_2	2048 (s), 2018 (s)
			C_6H_6	2043 (s), 2014 (s)
			KBr	2047 (s), 2016 (s)
2f	Me	Me	C_6H_6	2088 (s)

C1–N distance (1.177 Å), whereas the neopentyl isonitrile displays a bent C–N–R linkage (166.8°) and a shorter C1–N distance (1.159 Å). Tables I and II give positional parameters, and Table III gives selected distances and angles.

The IR spectra of complexes **2a–f** are all predicted to exhibit only one absorption from the isonitrile stretch in the region between 2000 and 2500 cm^{-1}. However, multiple absorptions are observed for complexes **2c–e**, and the number and the intensity of absorptions in some instances vary with the medium in which the spectrum is taken (Table IV). For example, the spectrum of **2c** in methylene chloride exhibits a strong band at 2067 cm^{-1} and two weak bands at 2035 and 1986 cm^{-1}. In a nonpolar, noncoordi-

Table V. UV–Vis Spectra of 2a–f in C_6H_6

	PR_3	isonitrile	λ, nm (ε, M^{-1} cm^{-1})
2a	Me	neopentyl	366 (7 400), 304 (12 200)
2b	Et	neopentyl	375 (10 000), 309 (19 400)
2c	*i*-Pr	neopentyl	375 (6 600), 306 (20 200)
2d	Me	2,6-xylyl	381 (6 300), 308 (17 000)
2e	*i*-Pr	2,6-xylyl	366 (5 700), 303 (11 700)
2f	Me	Me	368 (15 000), 304 (30 000)

Table VI. ^{1}H NMR Chemical Shifts for Ligand-Exchange Reactions[a]

2a	**2a** + 1 equiv of CNR[b]	**2a** + 1.5 equiv PR_3[c]
0.727 (s)	0.727 (br s)	0.723 (br s)
1.315 (pseudo t)	1.354 (br s)	1.030 (br s)
2.645 (s)	2.803 (br s)	2.634 (br s)

2c	**2c** + 2 equiv of CNR[b]	**2c** + 2 equiv of PR_3[d]
0.687 (s)	0.700 (br s)	0.687 (s)
1.397 (dt)	1.245 (br s)	1.397 (dt)
2.617 (m)	1.38 (br s)	2.617 (m)
2.825 (s)	2.70 (br s)	2.825 (s)
		1.055 (dd)
		1.685 (hept of d)

[a] C_6D_6. [b] Neopentyl isocyanide. [c] Trimethylphosphine. [d] Triisopropylphosphine.

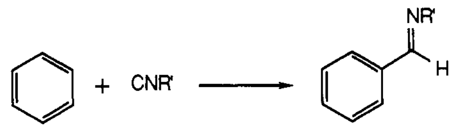
nating solvent such as hexane or pentane, all of the bands shift slightly (as might be expected), but the two lower energy absorptions are very intense. In the solid-state (KBr) spectrum of **2c**, the highest energy absorption remains unchanged from that of the spectrum in hexane, but the two low-energy absorptions are weak in intensity; behavior similar to that observed in methylene chloride. The $\nu_{C=N}$ bands for the xylyl isocyanide complexes are shifted to lower energy than their neopentyl isocyanide analogues, consistent with the stronger π-acceptor character of this isonitrile.

Multiple absorptions of this type witnessed in solution spectra of **2c** can normally be attributed to the presence of two (or more) isomers or a group effect such as molecular stacking. The first possibility is eliminated in this case because the IR spectrum of the closely related complex **2e** exhibits strong intensity multiple absorptions even in the solid state, where the X-ray structure shows only one (trans) isomer with single orientation of the isonitrile. The second possibility seems unlikely as examination of a series of spectra of **2c** in hexane solution where the concentration was varied from 2 to 18 mM showed that neither the energy of absorption nor the relative intensity of the bands displays any concentration dependence. Multiple splittings of the IR spectra of other isonitrile complexes are documented in the literature.[15]

The UV–vis spectra of **2a–f** show two absorptions in the regions of 370 and 306 nm (Table V). Due to the large magnitude of the extinction coefficients, these bands are assigned as MLCT bands. The electronic structure of these complexes are undoubtedly similar to that of $RhCl(CO)(PPh_3)_2$, which has been examined in detail by Gray et al.[16]

The $^{31}P\{^1H\}$ NMR spectra of **2a–f** each possess a single resonance which is split into a doublet due to coupling of phosphorus to rhodium. The phosphorus nuclei become less shielded (exhibit a downfield chemical shift) as the steric bulk of the alkyl group attached to phosphorus increases. The magnitude of the phosphorus–rhodium coupling is similar to that observed for the analogous carbonyl complexes[17] and increases (122–129 Hz) as the size of the phosphine alkyl substituent is varied from methyl to isopropyl.

Photochemical Reactions of 2a–c in Benzene. A sealed NMR tube containing a 2.5 mM solution of **2a** in benzene-d_6 was irradiated with high intensity 200-Watt Xe–Hg light (Pyrex filtered). The ^{1}H NMR spectrum of the sample taken after 90 min of irradiation showed a large number of new resonances in the region δ 0.5–1.5. Among the major new resonances were peaks at δ 1.02 and 3.24, which correspond to the benzaldimine product **5a**-d_6 (eq 2). Further confirmation of the formation of **5a**-d_6 was obtained from the GC/MS analysis of the final product mixture after 5 h of irradiation (M^+ = 181). The retention time of the major peak in the GC was identical with that of an authentic sample of **5a**.



(2)

5	R'
a	neopentyl
b	2,6-xylyl
c	methyl

The change in concentration of **2a** and **5a**-d_6 was monitored by taking ^{1}H NMR spectra at various intervals during the photolysis. The concentration versus time data revealed that, although the concentration of **2a** had decreased to less than 15% of its initial value during 210 min of irradiation, only a small amount of **5a**-d_6 had formed (less than 5% conversion of **2a**, Table IV). The large number of unidentifiable resonances in the ^{1}H NMR spectrum indicated that the majority of the complex underwent photochemical decomposition under these conditions. There was no evidence in the ^{1}H NMR spectrum for the formation of the di-μ-chlorotetrakis(trialkylphosphine)dirhodium(I) (**6**), although the formation of mixed-ligand dimers of this type cannot be excluded.

Complexes **2b,c** undergo a similar reaction to produce **5a**-d_6 when irradiated in benzene-d_6 solution. After 210 min of photolysis, **2b** gave 16% **5a**-d_6 at the expense of 46% of the starting complex, whereas **2c** gave 21% **5a**-d_6 at the expense of 33% of the starting material. Although the formation of undesirable byproducts occurs to a lesser extent with **2b,c**, the rate of formation of **5a**-d_6 is still extremely slow when compared to that of the $Fe(PR_3)_2(CNR)_3$ complexes mentioned previously. Surprisingly, **2d,e** did not produce any of the corresponding isonitrile insertion product **5b**-d_6 upon irradiation in C_6D_6. The presence of a more strongly bound isonitrile, as revealed by the X-ray and IR studies, must contribute to the prevention of the desired insertion reaction.

Reactions of 2a–c in Benzene in the Presence of Excess Isonitrile: Thermal Exchange Reactions. A series of ^{1}H NMR spectra were obtained of the complexes in benzene-d_6 solutions to which excess ligand had been added (either neopentyl isocyanide or trialkylphosphine) to see if ligand exchange at the metal center was rapid on the ^{1}H NMR time scale at room temperature. Although such experiments provide no information about the

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(15) See: Belt, S. T.; Duckett, S. B.; Haddleton, D. M.; Perutz, R. N. *Organometallics* **1989**, *8*, 748–759. Boeyens, J. C. A.; Coville, N. J.; Soldenhoff, K. *S. Afr. J. Chem.* **1984**, *37*, 153–160. Harris, G. W.; Albers, M. O.; Boeyens, J. C. A.; Coville, N. J. *Organometallics* **1983**, *2*, 609–614. Harris, G. W.; Boeyens, J. C. A.; Coville, N. J. *J. Organomet. Chem.* **1983**, *255*, 87–94.

(16) Brady, R.; Flynn, B. R.; Geoffroy, G. L.; Gray, H. B.; Peone, J.; Baska, L. *Inorg. Chem.* **1976**, *15*, 1485–1488.

(17) Browning, J.; Goggin, P. L.; Goodfellow, R. J.; Norton, M. G.; Rattray, A. J.; Taylor, B. F.; Mink, J. *J. Chem. Soc., Dalton Trans.* **1977**, 2061–2067.

Scheme I

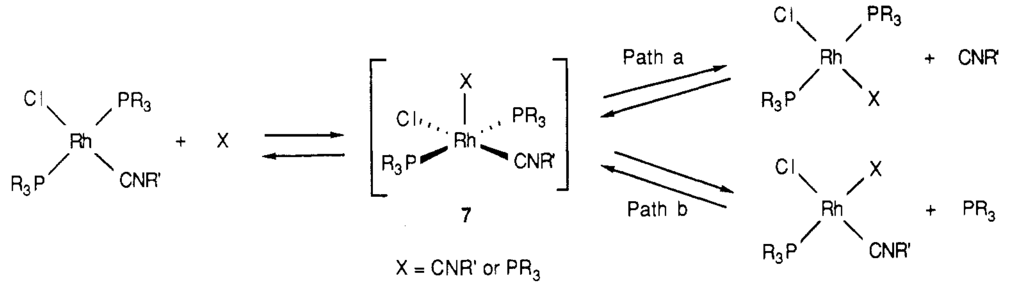

Table VII. Yields for Catalytic Reactions of 2a–c

entry	cat.	["Rh"]	[CNR][a]	irrad time, h	% conv[b]	turnovers
1	**2a**	0.2	1.0	16	62 (7)	3.7 (4)
2	**2b**	0.2	1.0	16	33 (3)	2.0 (2)
3	**2c**	0.2	1.0	16	76 (6)	4.5 (4)
4	**2c**	0.05	1.0	16	27 (1)	5.9 (2)
5	**2c**	0.05	0.5	16	68 (5)	7.7 (5)
6	**2c**	0.2	1.0	2	20 (3)	1.2 (1)
7	**2c**	0.2	1.0	4	35 (1)	2.1 (1)
8	**2c**	0.2	1.0	8	53 (5)	3.2 (3)
9	**2c**	0.2	1.0	12	60 (2)	3.6 (1)
10	**2c**	0.2	1.0	16	59 (3)	3.6 (2)
11	**2c**	0.2	1.0	20	64 (3)	3.8 (2)
12a	**2c**	0.2	1.0 mM of **5a**	16	97 (4)	
12b			1.0 mM of **5a**	16	94 (5)	
13	**10**	0.2	1.0	16	58 (3)	3.5 (2)
14	**2c**	0.2	1.0	9	45 (4)	2.2 (1)
15	**2c**	0.2	1.0 (1 atm of CO)	9	47 (1)	2.8 (1)
16	**2c**	0.2	2.0	4	25 (2)	1.3 (1)
17	**2c**	0.2	3.0	4	8 (1)	0.5[c]
18	**2c**	0.2	1.0 (1.0 mM PR_3)[d]	4	3.4 (2)	0.2[c]
19	**2c**	0.2	1.0 (2.0 mM PR_3)[d]	4	2.8 (3)	0.2[c]

[a] Neopentyl isocyanide unless otherwise indicated. [b] Based on total isonitrile present (metal bound and free) going to form **5**. [c] Error in this case was too small to be reported. [d] Triisopropylphosphine.

mechanism of the photochemically induced reaction in eq 2, they can give insight into the nature of the catalyst in solution prior to photolysis.

When 1 equiv of neopentyl isocyanide is added to a 5 mM solution of **2a** in benzene-d_6, the ^1H NMR spectrum of the mixture shows broadening of all of the resonances. Similar signal broadening is observed when excess trimethylphosphine (1.5 equiv/Rh) is added to a 5 mM solution of **2a** in d_6-benzene. The ^1H NMR data for both experiments are summarized in Table VI.

To determine if this phenomenon was general for this series of complexes, the experiments described above were repeated using **2c** with excess neopentyl isocyanide or triisopropylphosphine. Although the experiment involving a benzene solution of **2c** in the presence of excess isonitrile shows dynamic behavior similar to that observed with **2a**, the ^1H NMR spectrum of **2c** in the presence of triisopropylphosphine shows no evidence of signal broadening, and separate resonances for free and bound triisopropylphosphine (along with their expected H–P coupling) are clearly visible (Table VI).

As alluded to above, in the three out of four experiments where ^1H NMR signal broadening is seen, a rapid ligand-exchange process is occurring at room temperature (Scheme I). The exchange probably occurs via an associative mechanism involving the pentacoordinate intermediate 7. Apparently, the steric bulk of free triisopropylphosphine, combined with the bulk of the *trans*-triisopropylphosphines already attached to the metal, makes it impossible to form the necessary square-pyramidal intermediate of type 7, and hence no ligand exchange is observed. It was not possible to determine from these experiments if the initial exchange involves replacement of metal-bound isonitrile or phosphine (pathways a and b, respectively, of Scheme I) or a mixture of both processes. It should be noted that this process can be observed only under conditions where the concentration of both the complex and the free ligand are kept very low. It was discovered that at higher concentrations (>5 mM) the isonitrile undergoes reaction with the complex to generate a product that is insoluble in benzene. A discussion of the reaction chemistry of this product, identified as **3a**, will be deferred until later.

Reactions of 2a–f in Benzene in the Presence of Excess Isonitrile: Catalytic Reactions. The reaction in eq 2 can be made catalytic by irradiating complexes **2a–c** in the presence of excess isonitrile under dilute conditions. When a 0.2 mM solution of **2a** in benzene containing 5 equiv of neopentyl isocyanide was irradiated for 16 h, 62% of the total isonitrile present at the beginning of the reaction was converted to **5a** (Table VII, entry 1). Similar reactions in which **2b** and **2c** were used as the catalyst resulted in isonitrile conversions of 33% and 76%, respectively (Table VII, entries 2 and 3).

When the formation of **5a** was monitored as a function of time, it was discovered that the complete conversion of isonitrile did not occur and that the formation of **5a** ceased after about 12 h (entries 6–11). A reaction in which a benzene solution containing **5a** (1.0 mM) and **2c** (0.2 mM) was irradiated for 16 h revealed that the incomplete conversion of isonitrile was not the result of the system being at thermal equilibrium or at some type of photostationary state (entry 12). An electronic absorption spectrum of a reaction taken after 12 h of irradiation indicated that the catalyst was being removed from solution.

As mentioned previously, the reaction of **2c** with excess isonitrile (2 equiv) at moderate isonitrile concentrations resulted in the formation of an insoluble product. The

Table VIII. Positional Parameters and *B*(eq) Values for $\{Rh[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)_2\}Cl$

atom	*x*	*y*	*z*	*B*(eq), Å^2
Rh	0.38680 (6)	0.19290 (6)	0.12993 (3)	3.25 (3)
Cl	0.0890 (3)	0.1321 (2)	0.8811 (1)	6.7 (2)
P1	0.1998 (2)	0.1326 (2)	0.1206 (1)	3.5 (1)
P2	0.5697 (2)	0.2600 (2)	0.1394 (1)	3.5 (1)
N1	0.3841 (7)	0.1820 (6)	0.2642 (4)	5.1 (5)
N2	0.3960 (7)	0.1833 (8)	-0.0034 (4)	6.8 (5)
C1	0.3852 (7)	0.1851 (8)	0.2142 (4)	4.3 (5)
C2	0.381 (1)	0.192 (1)	0.3269 (5)	7.0 (7)
C3	0.399 (1)	0.0981 (9)	0.3596 (4)	5.4 (7)
C4	0.511 (1)	0.056 (1)	0.3446 (7)	12 (1)
C5	0.302 (1)	0.031 (1)	0.3440 (5)	8.0 (8)
C6	0.398 (2)	0.124 (1)	0.4233 (5)	13 (1)
C7	0.3926 (7)	0.1903 (8)	0.0455 (4)	4.5 (5)
C8	0.387 (1)	0.1587 (8)	-0.0665 (5)	6.4 (7)
C9	0.408 (1)	0.2463 (9)	-0.1039 (4)	5.1 (6)
C10	0.322 (1)	0.321 (1)	-0.0859 (7)	10 (1)
C11	0.384 (1)	0.219 (1)	-0.1655 (5)	12 (1)
C12	0.531 (1)	0.284 (1)	-0.0933 (5)	7.6 (7)
C13	0.1954 (8)	0.0016 (7)	0.1155 (5)	4.8 (6)
C14	0.259 (1)	-0.0460 (8)	0.1686 (5)	7.0 (7)
C15	0.248 (1)	-0.0337 (8)	0.0610 (5)	7.2 (7)
C16	0.1185 (8)	0.1761 (9)	0.0553 (4)	5.0 (6)
C17	0.118 (1)	0.284 (1)	0.0493 (5)	7.3 (7)
C18	0.0003 (9)	0.132 (1)	0.0420 (4)	7.2 (7)
C19	0.1167 (9)	0.1590 (8)	0.1843 (4)	4.8 (6)
C20	0.115 (1)	0.2653 (8)	0.2013 (5)	6.6 (7)
C21	-0.004 (1)	0.1182 (8)	0.1866 (5)	6.4 (7)
C22	0.593 (1)	0.3338 (8)	0.2057 (4)	5.0 (6)
C23	0.496 (1)	0.4058 (9)	0.2138 (5)	8.7 (9)
C24	0.709 (1)	0.381 (1)	0.2157 (5)	9.2 (9)
C25	0.607 (1)	0.3325 (8)	0.0762 (4)	5.7 (7)
C26	0.730 (1)	0.367 (1)	0.0718 (5)	8.3 (8)
C27	0.524 (1)	0.415 (1)	0.0673 (5)	8.7 (8)
C28	0.6830 (8)	0.1689 (8)	0.1445 (6)	5.5 (6)
C29	0.683 (1)	0.109 (1)	0.0893 (7)	9 (1)
C30	0.675 (1)	0.105 (1)	0.1975 (7)	10 (1)

Table IX. Selected Distances (Å) and Angles (deg) for $\{Rh[P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)_2\}Cl$

bond	dist	bonds	angle
Rh-P1	2.332 (3)	P1-Rh-P2	177.4 (1)
Rh-P2	2.325 (3)	P1-Rh-C1	91.1 (3)
Rh-C1	1.95 (1)	P1-Rh-C7	88.7 (3)
Rh-C7	1.95 (1)	P2-Rh-C1	88.8 (3)
C1-N1	1.15 (1)	P2-Rh-C7	91.6 (3)
N1-C2	1.45 (1)	C1-Rh-C7	175.5 (4)
C7-N2	1.13 (1)	Rh-C1-N1	179 (1)
N2-C8	1.49 (1)	C1-N1-C2	172 (1)
		Rh-C7-N2	176 (1)
		C7-N2-C8	170 (1)

product was purified by recrystallization from a hexane/methylene chloride solvent mixture and identified as **3a** by NMR, IR, elemental analysis, and single-crystal X-ray diffraction (Figure 3). Pertinent structural data are given in Tables VIII and IX.

Although no precipitates were ever observed in any of the catalytic studies, it seemed possible that the slow formation of **3a** could be deactivating the catalytic cycle by removing the catalyst from solution. To test this hypothesis, a slurry of **3a** (4 mg) in 25 mL of a 1 mM solution of neopentyl isocyanide in benzene was irradiated for 16 h. Surprisingly, during the first few hours of irradiation it was observed that **3a** slowly went into solution. GC analysis of the final reaction mixture showed that the conversion of isonitrile to **5a** was 58% (Table VII, entry 13). It is evident that the formation of **3a** is not a route to irreversible catalyst deactivation. It appears that **3a** possesses trace solubility in benzene and can be converted via photolysis to a catalytically active species. Preparation of the PF_6^- salt of this complex (**3b**) was accomplished by metathesis with $Na^+PF_6^-$ in acetone. This salt was found to be inactive as a catalyst, suggesting that the presence of chloride ion is important for the formation of the catalytically active species. The ultimate mode of catalyst deactivation in this system remains unidentified. NMR spectroscopic analysis of the solutions at the end of the reaction show no identifiable (or major) compounds.

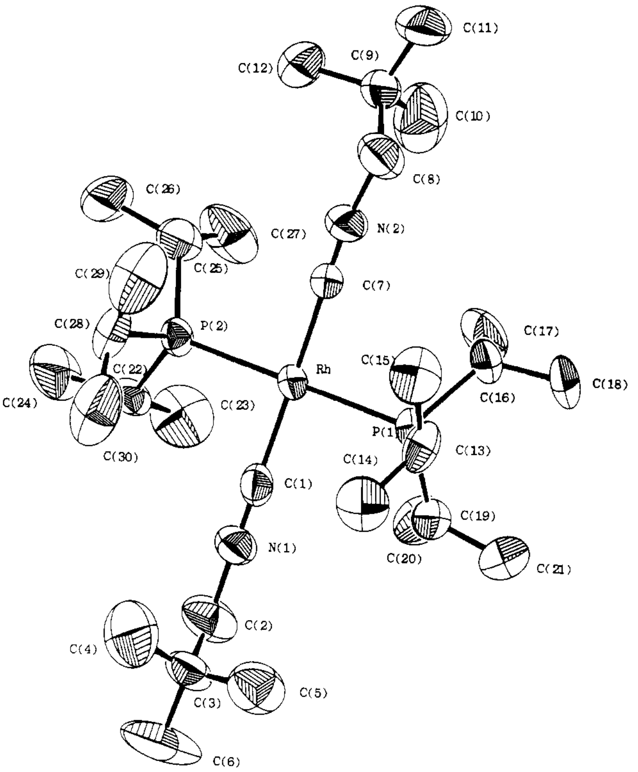

Figure 3. ORTEP diagram of $\{Rh(P(i\text{-}Pr)_3]_2(CNCH_2CMe_3)_2\}Cl$. Ellipsoids are shown at the 50% level.

Complexes **2d,e** were irradiated with excess 2,6-xylyl isocyanide under the standard catalytic conditions to see if changing the isonitrile effected the insertion reaction. None of the expected aldimine product **5b** was detected by GC after 16 h of irradiation.

Earlier work in our group involving the catalysis of the reaction in eq 2 using $Cp^*Rh(CNR)_2$ showed a rate enhancement when the reaction was carried out in the presence of carbon monoxide.[18] In contrast, when the analogous reaction using **2c** as the catalyst was performed with CO, no increase in the rate of formation of **5a** was observed (Table VI, entries 14, 15).

To obtain crude mechanistic information about the photochemical step in the catalytic process, a series of reactions was conducted in which the production of **5a** was measured as a function of the amount of excess isonitrile or phosphine introduced at the beginning of the reaction. The results indicate that the rate of reaction is only slightly affected by moderate increases in the concentration of isonitrile (Table VII, entries 7, 16, 17) but that the addition of free triisopropylphosphine has a dramatic effect on the production of **5a** (entries 7, 18, 19). The suppression observed in the cases where excess phosphine was added suggests that phosphine dissociation is the predominant photochemical step leading to product (Scheme IIa). This seems reasonable since dissociation of phosphine from **2a–c** would produce a high-energy 14-electron intermediate, which upon oxidative addition of benzene would result in the formation of a complex still possessing a coordinated isonitrile ligand. Such an intermediate could then im-

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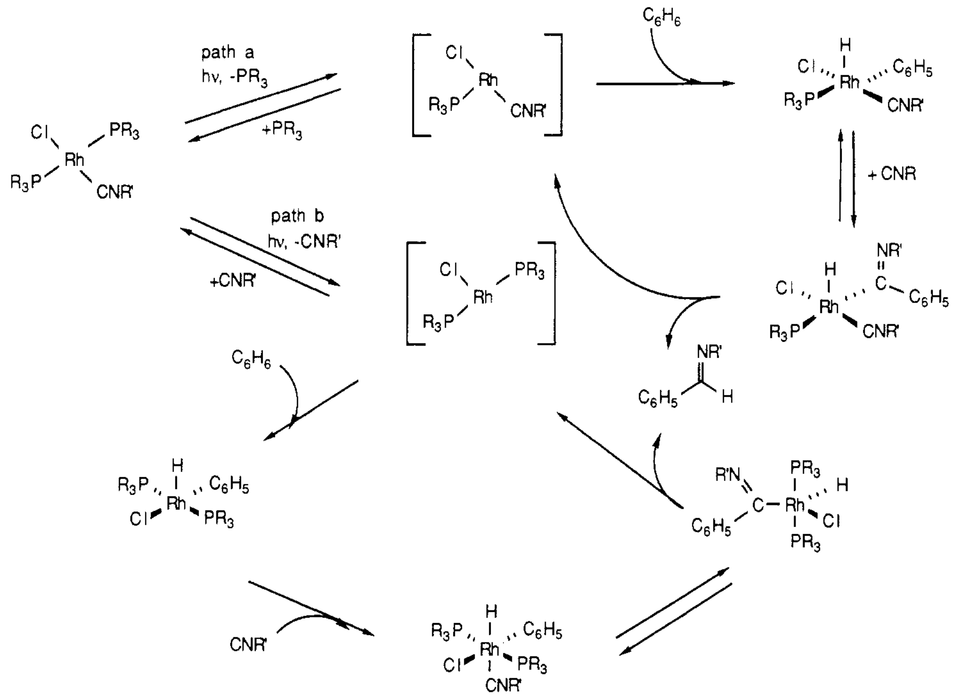
[18] Jones, W. D.; Duttweiler, R. P.; Feher, F. J.; Hessell, E. T. *Nouv. J. Chim.* **1989**, *13*, 725–736.

Scheme II



mediately insert the isonitrile into the metal–carbon bond, the insertion being driven by phosphine recoordination.

In an alternative mechanism, photochemical dissociation of isonitrile followed by benzene oxidative addition would give an aryl hydride intermediate. This species would then need to recoordinate isonitrile prior to insertion (Scheme IIb). Credence for this pathway is provided by Werner's observations of the reaction of benzene with the iridium analogue $Ir[P(i\text{-}Pr)_3]_2Cl$ to give $Ir[P(i\text{-}Pr)_3]_2(Ph)(H)Cl$.[19] This species then reacts with added CO to give an octahedral complex. In this pathway, the inhibition of aldimine formation by added phosphine would be explained by the formation of $RhCl[P(i\text{-}Pr)_3]_3$.

It is possible that isonitrile dissociation is a facile process but that only an intermediate derived from phosphine dissociation (containing a coordinated isonitrile) goes on to produce **5a**. In studies of $RhCl(CO)(PPh_3)_2$, Geoffrey observed phosphine inhibition of oxidation reactions and suggested photochemical phosphine dissociation.[20] Later flash photolysis studies by Ford, however, provide strong evidence that CO dissociation is the primary photochemical reaction.[21]

When a catalytic photolysis experiment was attempted using complex **2c** (0.2 mM) in a 1.0 mM solution of neopentyl isocyanide in pentane, none of the products that would have resulted from isonitrile insertion into the C–H bonds of pentane were observed. When the experiment was repeated, it was noticed that a fine precipitate forms (presumed to be **3a**) upon mixing of the stock solutions used in the sample preparation. Apparently, the photochemical reaction that converts **3a** to an active catalyst does not occur in pentane.

Conclusions

A new class of square-planar rhodium(I) isonitrile complexes has been synthesized and characterized. The complexes catalyze the insertion of isonitrile into the C–H bonds of benzene under dilute conditions cleanly and in good yield but at very slow rates. It is not exactly known at this time why the complexes fail to insert isonitrile into the C–H bonds of alkanes, although it is possible that the presence of the isonitrile ligand on the metal center could significantly decrease the ability of the rhodium to activate the C–H bonds of alkanes. However, while this work was in progress, Tanaka reported that $RhCl(PBu_3)_2(CO)$ is capable of catalyzing isonitrile insertion into the C–H bonds of saturated hydrocarbons.[22] Presumably, the Tanaka complex and **2** should form similar complexes in the presence of excess isonitrile in solution. The discrepancy between these two independent sets of results remains unexplained.

Experimental Section

All operations and routine manipulations were performed under a nitrogen atmosphere, either on a high-vacuum line using modified Schlenk techniques or in a Vacuum Atmospheres Corp. Dri-Lab. Tetrahydrofuran, diethyl ether, benzene, and toluene were distilled from dark purple solutions of benzophenone ketyl. Hexane and pentane were stirred over concentrated sulfuric acid for 24 h and washed successively with potassium permanganate in 10% aqueous sulfuric acid, water, and saturated aqueous sodium carbonate. The resulting olefin-free hydrocarbons were predried over calcium chloride before being distilled from dark purple solutions of benzophenone ketyl. Benzene-d_6, THF-d_8, and toluene-d_8 were distilled under vacuum from dark purple solutions of benzophenone ketyl and stored in samples with Teflon-sealed vacuum line adapters. Benzene-d_6 was also stored in a bottle in a Vacuum Atmospheres Dri-Lab exclusively used for NMR sample preparation, eliminating the possibility of contamination of the NMR samples by other solvent vapors. Acetone-d_6 was freeze–pump–thaw degassed, dried over 4A molecular sieves, and stored in an ampule with a Teflon-sealed vacuum line adapter.

Di-μ-chlorotetrakis(ethylene)dirhodium(I) was prepared according to a literature method[23] and used immediately. Trimethylphosphine was purchased from Strem Chemicals, Inc., distilled at room temperature under vacuum, and stored in an

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(19) Werner, H.; Höhn, A.; Dziallas, M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1090–1092.

(20) Geoffroy, G. L.; Denton, D. A.; Keeney, M. E.; Bucks, R. R. *Inorg. Chem.* **1976**, *15*, 2382–2385.

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(22) Tanaka, M.; Sakakura, T.; Tokonuga, Y.; Sodeyama, T. *Chem. Lett.* **1987**, 2373–2374.

(23) Cramer, R. *Inorg. Synth.* **1974**, *15*, 14–16.

ampule with a vacuum line adapter. Triethylphosphine, triisopropylphosphine, tri-*tert*-butylphosphine, and 2,6-xylyl isocyanide were purchased from Strem Chemicals, Inc., and used without further purification. Neopentyl isocyanide,[24] methyl isocyanide,[25] and 2,2-dimethyl-5-phenyl-4-aza-4-pentene[26] were prepared according to literature procedures.

^{1}H (400 MHz) and ^{31}P (162 MHz) NMR spectra were recorded on a Bruker WH-400 NMR spectrometer. The chemical shifts of the ^{1}H NMR spectra were reported in units of δ (ppm) relative to tetramethylsilane by using the residual resonances of the deuterated solvent as the internal reference (C_6D_6, δ 7.150; THF-d_8, δ 1.730; acetone-d_6, δ 2.06). The chemical shifts of the ^{31}P spectra were reported in units of δ (ppm) relative to 30% H_3PO_4. ^{13}C (75 MHz) spectra were recorded on a GE-300MHz NMR spectrometer. The chemical shifts of the ^{13}C NMR spectra are reported in units of δ (ppm) relative to tetramethylsilane using the solvent peak as an internal reference (C_6D_6, δ 128.0).

Infrared spectra were recorded on a Mattson Instruments, Inc., Sirius 100 infrared spectrometer. Analytical gas chromatography was conducted on a Hewlett-Packard 5710A gas chromatograph using a Supelcowax 10 glass capillary column and flame-ionization detector. Ultraviolet–visible spectra were recorded on a Perkin-Elmer Lambda Array 3840 spectrometer in concert with an IBM personal computer with 0.5-mm path length quartz cells. Mass spectral analyses were conducted on a Nermag R10-10c combination GC/MS. All photolysis experiments were performed using a high-pressure 200-W mercury lamp (Hanovia 831691). Preparative thin-layer chromatography was performed on commercial glass plates (EM Scientific) of silica gel (2-mm thickness). Analyses were obtained from Desert Analytics. X-ray diffraction studies were carried out on an Enraf-Nonius CAD4 diffractometer.

Chloro(neopentyl isocyanide)bis(trimethylphosphine)rhodium(I) (2a). Trimethylphosphine (115 mm, 0.123 L, 298 K, 0.76 mmol) was added by distillation on a high-vacuum line at 77 K to a solution of 233 mg (0.57 mmol) of di-μ-chlorotetrakis(ethylene)dirhodium(I) in 10 mL of a 1:1 hexane:THF solvent mixture. The mixture was warmed to room temperature and stirred for 2 h. Two further portions of trimethylphosphine (of equal quantity of the first) were added in an analogous manner at 1-h intervals, and the resulting reaction mixture was stirred for 6 h. The mixture was removed from the vacuum line and placed in a drybox. A solution of 137 μL (111 mg, 1.15 mmol) of neopentyl isocyanide in 2 mL of hexane was added dropwise to the reaction mixture, and the resulting yellow solution was stirred for 18 h at room temperature. The reaction mixture was filtered and concentrated to one-third of the original volume. Prolonged cooling of this solution at −20 °C resulted in the formation of yellow platelets, which when isolated by filtration gave 300 mg (68%) of product: ^{1}H NMR (C_6D_6) δ 0.727 (s, 9 H, $C(CH_3)_3$), 1.315 (pseudo t, J = 2.7 Hz, 18 H, *trans*-$P(CH_3)_3$), 2.645 (s, 2 H, NCH_2); ^{13}C NMR (C_6D_6) δ 16.1 (q, J_{CH} = 130 Hz, $P(CH_3)_3$), 26.4 (q, J_{CH} = 126 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$), 31.3 (s, $C\mathrm{(CH_3)_3}$), 55.8 (t, J_{CH} = 145 Hz, NCH_2), 158.1 (d, J_{CRh} = 64 Hz, CNR); ^{31}P NMR (C_6D_6) δ −9.81 (d, J_{PRh} = 123 Hz); MS (35 eV), m/z 387 (M^+), 311 (M^+ − PMe_3), 290 (M^+ − CNR), 254 (M^+ − CNR − Cl). Anal. Calcd (found) for $C_{12}H_{29}ClNP_2Rh$: C, 37.18 (37.13); H, 7.54 (7.56); N, 3.61 (3.59).

Chloro(neopentyl isocyanide)bis(triethylphosphine)rhodium(I) (2b). To a stirred solution of 211 mg (0.54 mmol) of di-μ-chlorotetrakis(ethylene)dirhodium(I) in 10 mL of a 1:1 hexane:THF solvent mixture was added dropwise a solution of 255 mg (319 μL, 2.16 mmol) of triethylphosphine in 2 mL of hexane. A light precipitate formed during the addition of the phosphine, but the reaction mixture became homogeneous upon stirring overnight.

To the orange–yellow solution was added dropwise a solution of 102 mg (126 μL, 1.06 mmol) of neopentyl isocyanide in 3 mL of hexane. The solution was stirred for 8 h, and then the solvent was removed in vacuo to give 409 mg (82%) of a waxy yellow solid, which was spectroscopically (NMR) pure. A small sample was further purified for elemental analysis by preparative TLC (4:1 hexane:THF). The ^{1}H and ^{31}P NMR spectra of the TLC product were identical with those of the crude product. The product was a yellow liquid: ^{1}H NMR (C_6D_6) δ 0.732 (s, 9 H, $C(CH_3)_3$), 1.163 (quintet, 18 H, J = 7.6 Hz, $\mathrm{PCH_2C}H_3$), 1.830 (m, 12 H, $\mathrm{PC}H_2\mathrm{CH_3}$), 2.710 (s, 2 H, NCH_2); ^{13}C NMR (C_6D_6) δ 8.6 (dq, J_{CH} = 126 Hz, J_{CP} = 12 Hz, $\mathrm{PCH_2}C\mathrm{H_3}$), 17.0 (tt, J_{CH} = 133 Hz, J_{CP} = 8 Hz, PCH_2CH_3), 26.5 (q, J_{CH} = 127 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$), 31.2 (s, $C\mathrm{(CH_3)_3}$), 56.0 (t, J_{CH} = 145 Hz, NCH_2), 158.8 (d, J_{CRh} = 69 Hz, CNR); ^{31}P NMR (C_6D_6) δ 24.28 (d, J_{PRh} = 126 Hz). Anal. Calcd (found) for $C_{18}H_{41}ClNP_2Rh$: C, 45.82 (46.20); H, 8.76 (8.99); N, 2.97 (2.77).

Chloro(neopentyl isocyanide)bis(triisopropylphosphine)rhodium(I) (2c). The synthesis of complex **2c** was identical with that of **2b** except that 354 mg (440 μL, 2.21 mmol) of triisopropylphosphine was substituted for triethylphosphine. The crude product was extracted into 20 mL of hexane and filtered to remove insolubles (approximately 17 mg of a pale yellow solid). The filtrate was evaporated in vacuo to yield 495 mg (80%) of a yellow–orange solid. The product is stable in air and benzene solution and can be recrystallized from hexane at −20 °C; ^{1}H NMR (C_6D_6) δ 0.687 (s, 9 H, $C(CH_3)_3$), 1.397 (dt, 36 H, J_{HH} = J_{HP} = 7.0 Hz, $\mathrm{PCH(C}H_3\mathrm{)_3}$), 2.617 (m, 6 H, PCH), 2.825 (s, 2 H, NCH_2); ^{13}C NMR (C_6D_6) δ 20.0 (qd, J_{CH} = 122 Hz, J_{CP} = 8 Hz, $\mathrm{PCH(}C\mathrm{H_3)_3}$), 24.0 (dt, J_{CH} = 131 Hz, J_{CP} = 10 Hz, PCH), 26.5 (qd, J_{CH} = 122 Hz, J_{CP} = 8 Hz, $\mathrm{C(}C\mathrm{H_3)_3}$), 30.9 (s, $C\mathrm{(CH_3)_3}$), 56.5 (t, J_{CH} = 140 Hz, NCH_2), 161 (dt, J_{CRh} = 67 Hz, J_{CP} = 16 Hz, CNR); ^{31}P NMR (C_6D_6) δ 47.43 (d, J_{PRh} = 129 Hz); MS (40 eV), m/z 555 (M^+), 396 (M^+ − PR_3). Anal. Calcd (found) for $C_{24}H_{53}ClNP_2Rh$: C, 51.84 (51.84), H, 9.61 (9.85), N, 2.52 (2.56).

Chloro(2,6-xylyl isocyanide)bis(trimethylphosphine)rhodium(I) (2d). A flask containing 44 mg. (0.11 mmol) of di-μ-chlorotetrakis(ethylene)dirhodium(I) in 3 mL of THF was cooled to 77 K, and 164 mm (0.051 L, 0.45 mmol, 298 K), of PMe_3 was distilled in under reduced pressure. The mixture was allowed to warm to room temperature and stirred for 1.5 h. To the solution was added 29 mg (0.22 mmol) of 2,6-xylyl isocyanide. The resulting solution was stirred for 30 min, and then the solvent was removed in vacuo to give 33 mg (35%) of yellow–orange solid: ^{1}H NMR (C_6D_6) δ 1.273 (pseudo t, 18 H, J_{HP} = 2.9 Hz, $P(CH_3)_3$), 2.290 (s, 6 H, aryl CH_3), 6.786 (s, 3 H, aryl H); ^{13}C{^{1}H} NMR (C_6D_6, 75 MHz) δ 16.1 (pseudo t, J_{CP} = 12 Hz, $\mathrm{P(}C\mathrm{H_3)_3}$), 19.3 (s, $\mathrm{Ar(}C\mathrm{H_3)_2}$), 125.8 (s, Ar C), 127.9 (s, Ar C), 136.5 (s, Ar C) (the isonitrile carbon and one of the aryl carbons were not observed); ^{31}P NMR (C_6D_6) δ −11.22 (d, J_{P-Rh} = 122 Hz); MS (70 eV), m/z 421 (M^+), 309 (M^+ − PR_3 − Cl), 290 (M^+ − CNR′), 254 (M^+ − CNR′ − Cl − CH_3), 215 (M^+ − CNR′ − PR_3), 178 (M^+ − CNR′ − PR_3 − Cl). Anal. Calcd (found) for $C_{15}H_{27}ClNP_2Rh$: C, 42.7 (42.0); H, 6.5 (6.5); N, 3.3 (3.0).

Chloro(2,6-xylyl isocyanide)bis(triisopropylphosphine)rhodium(I) (2e). The synthesis of complex **2e** was similar to that of **2b** except that 132 mg (0.34 mmol) of di-μ-chlorotetrakis(ethylene)dirhodium(I) was used with 217 mg (270 μL, 1.36 mmol) of triisopropylphosphine and 89 mg (0.68 mmol) of 2,6-xylylisocyanide. After removal of the solvent in vacuo, the crude product was placed in 20 mL of benzene and filtered to remove any insoluble materials. The filtrate was evaporated in vacuo to give 233 mg (58%) of product as an orange–yellow solid. The product is air stable in solution and can be recrystallized from a hexane:THF solvent mixture; ^{1}H NMR (C_6D_6) δ 1.362 (dt, 36 H, J_{HH} = J_{HP} = 7.0 Hz, $\mathrm{PCH(C}H_3\mathrm{)_3}$), 2.355 (s, 6 H, $\mathrm{ArC}H_3$), 2.556 (m, 6 H, PCH), 6.748 (s, 3 H, Ar H); ^{13}C{^{1}H} NMR (C_6D_6) δ 18.8 (s, $\mathrm{Ar(}C\mathrm{H_3)_2}$), 20.2 (d, J_{CP} = 7 Hz, $\mathrm{PCH(}C\mathrm{H_3)_2}$), 24.4 (pseudo t, J_{CP} = 10 Hz, $\mathrm{P}C\mathrm{H(CH_3)_2}$), 27.2 (s, Ar C), 27.9 (s, Ar C), 133.0 (s, Ar C) (the isonitrile carbon and one of the aryl carbons were not observed); ^{31}P NMR (C_6D_6) δ 47.6 (d, J_{PRh} = 117 Hz). Anal. Calcd (found) for $C_{27}H_{51}ClNP_2Rh$: C, 54.96 (54.39); H, 8.71 (8.61); N, 2.37 (2.29).

Chloro(methyl isocyanide)bis(trimethylphosphine)rhodium(I) (2f). The synthesis of **2f** was identical with that of complex **2a** except that 290 mg (0.75 mmol) of di-μ-chlorotetrakis(ethylene)dirhodium(I) was used with three separate additions of trimethylphosphine (360 mm, 0.051 L, 298 K, 1.0 mmol) and 63 mg (80 μL, 1.5 mmol) of methyl isocyanide. The crude product was recrystallized from a toluene:hexane solvent mixture at −20 °C; ^{1}H NMR (C_6D_6) δ 1.286 (pseudo t, J_{HP} = 3 Hz, 18 H, $P(CH_3)_3$), 2.218 (s, 3 H, NCH_3); ^{13}C NMR (C_6D_6) δ 16.0 (q of m, J_{CH} = 130 Hz, $P(CH_3)_3$), 28.0 (q, J_{CH} = 143 Hz, NCH_3), 158.4 (br d, J_{CRh} = 68 Hz, CNR); ^{31}P{^{1}H} NMR (C_6D_6) −9.934 (d,

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(25) Schuster, R. E. *Org. Synth.* **1973**, *Coll. Vol. 5*, 772.

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Table X. Summary of Crystallographic Data

	2c	2e	3a
	Crystal Parameters		
formula	$RhClP_2NC_{24}H_{53}$	$RhP_2ClNC_{30}H_{54}$	$RhClP_2N_2C_{30}H_{64}$
cryst system	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (no. 14)	*Pnna* (no. 52)	$P2_1/n$ (no. 14)
Z	4	4	4
a, Å	13.894 (5)	14.620 (2)	11.633 (3)
b, Å	12.014 (6)	16.07 (2)	13.945 (3)
c, Å	18.896 (9)	15.358 (4)	23.050 (9)
β, deg	103.58 (4)	90.0	92.69 (2)
V, Å³	3066 (5)	3608 (5)	3735 (3)
d_{calc}, g/cm³	1.20	1.16	1.16
temp, °C	23	23	23
	Measurement of Intensity Data		
diffractometer		Enraf-Nonius CAD4	
radn (graphite monochr)		Mo, λ = 0.71073 Å	
scan type		$2\theta/\omega$	
scan rate, deg/min		2–16.5	
total background time		scan time/2	
takeoff angle, deg		2.6	
scan range, deg		0.7 + 0.35 tan (*θ*)	
2*θ* range, deg	2–44	2–50	2–44
data coll	$+h,+k,\pm l$	$+h,+k,+l$	$+h,+k,\pm l$
no. of data coll	3980	3571	4806
no. of unique data >3*σ*	3258	2036	2178
no. of parameters varied	262	175	325
abs coeff, cm⁻¹	7.43	6.40	6.21
systematic absences	0*k*0, *k* odd *h*0*l*, *l* odd	0*kl*, *k* + *l* odd *h*0*l*, *h* + *l* odd *hk*0, *h* odd	0*k*0, *k* odd *h*0*l*, *h* + *l* odd
abs corr	none	none	none
equiv data	$0kl = 0k\bar{l}$	none	$0kl = 0k\bar{l}$
agreement between equiv data (F_{obs}), %	0.2		0.9
R_1	0.032	0.029	0.042
R_2	0.047	0.042	0.045
GOF	1.62	1.26	1.09
largest peak in final e⁻ map	0.67	0.48	0.50

J_{PRh} = 123 Hz). Anal. Calcd (found) for $C_8H_{21}ClNP_2Rh$: C, 28.98 (29.20); H, 6.38 (6.46); N, 4.22 (4.35).

Attempted Synthesis of Chloro(neopentyl isocyanide)bis(*tri-tert*-butylphosphine)rhodium(I). The attempted synthesis was identical with that of **2b** except that 160 mg (0.41 mmol) of di-*μ*-chlorotetrakis(ethylene)dirhodium(I) was used with 332 mg (1.65 mmol) of tri-*tert*-butylphosphine and 80 mg (0.82 mmol) of neopentyl isocyanide. The solvent was removed from the reaction mixture in vacuo, and the residue was recrystallized from hexane at −20 °C to give 20 mg (approximately 8% yield) of red crystals tentatively identified as *trans*-di-*μ*-chlorobis(tri-*tert*-butylphosphine)bis(neopentyl isocyanide)dirhodium(I) (4): ^1H NMR (C_6D_6) δ 0.876 (s, 9 H, $C(CH_3)_3$), 1.618 (d, J_{HP} = 12 Hz, $C(CH_3)_3$), 2.771 (s, NCH_2); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 27.0 (s, $C(CH_3)_3$), 31.7 (s, $C(CH_3)_3$), 33.5 (s, $C(CH_3)_3$), 39.8 (d, J_{CP} = 14 Hz, $PC(CH_3)_3$), 56.7 (s, NCH_2); $^{31}P\{^1H\}$ NMR (C_6D_6) δ 49.5 (d, J_{PRh} = 191 Hz); IR (C_6D_6) 2101 cm⁻¹ (CNR).

Bis(neopentyl isocyanide)bis(triisopropylphosphine)rhodium(I) Chloride (3a). To a stirred solution of 65 mg (0.117 mmol) of **2c** in 3 mL of benzene was added dropwise 28 *μ*L (23 mg, 0.234 mmol) of neopentyl isocyanide. Upon addition of one-half of the isonitrile a yellow precipitate formed. The reaction mixture was stirred for 10 min, and then it was filtered to isolate the product (a yellow solid) in essentially quantitative yield. The product was recrystallized from a hexane:methylene chloride solvent mixture, giving bright yellow transparent crystals suitable for X-ray diffraction; ^1H NMR (d_6-acetone) δ 1.033 (s, 18 H, $NCH_2(CH_3)_3$), 1.392 (q, J_{HP} = 6.5 Hz, 36 H, $PCH(CH_3)_2$), 2.493 (br s, 6 H, PCH), 3.767 (s, 2 H, NCH_2); $^{31}P\{^1H\}$ NMR (d_6-acetone) δ 53.14 (d, J_{PRh} = 116 Hz); IR (CH_2Cl_2) 2126.4 cm⁻¹ (CNR). Anal. Calcd found for $C_{30}H_{64}ClN_2P_2Rh$: C, 55.17 (55.29); H, 9.88 (10.02); N, 4.29 (4.34).

Bis(neopentyl isocyanide)bis(triisopropylphosphine)rhodium(I) Hexafluorophosphate (3b). To a stirred solution of 50 mg (0.75 mmol) of **3a** in 3 mL of acetone was added 15 mg (0.75 mmol) of sodium hexafluorophosphate. The reaction mixture was stirred for 24 h at room temperature, and then it was filtered to remove insoluble sodium chloride. The residue was recrystallized from a hexane/methylene chloride solvent mixture to give the desired product as bright yellow crystals. The yield was not determined for this reaction; ^{31}P NMR (d_6-acetone) δ −11.52 (heptet, J_{PF} = 707 Hz), 53.14 (d, J_{PRh} = 115 Hz). Anal. Calcd (found) for $C_{30}H_{64}F_6N_2P_3Rh$: C, 47.25 (47.24); H, 8.46 (8.57); N, 3.67 (3.67).

Gas Chromatography Analyses of Aldimine Products. All gas chromatography analyses of 2,2-dimethyl-5-phenyl-4-aza-4-pentene were conducted at 120 °C isothermal. All concentrations reported for the almidine product were referenced to an internal standard of heptadecane (1.0 mM) and are the average of five injections). The response factor for 2,2-dimethyl-5-phenyl-4-aza-4-pentene vs heptadecane was obtained by taking the average peak ratio (heptadecane/aldimine) for five 3.5-*μ*L injections of a benzene solution that was 1.0 mM in concentration for both species. The peak integrations were determined by cut-and-weigh methods to an accuracy of 0.1 mg. The errors shown for the reported concentrations are a measure of the precision of the method and were calculated by standard methods.

General Procedure for Sample Preparation and Photolysis. All of the photolysis samples were prepared in a Vacuum Atmospheres Dri-Lab from stock benzene solutions of the appropriate rhodium complex and isonitrile. The preparation of a sample that was 1.0 mM in isonitrile and 0.2 mM in rhodium complex serves to illustrate the procedure.

To a 25-mL Pyrex volumetric flask was added 10 mL of a 5.0 × 10^{-4} M solution of rhodium complex in benzene and 10 mL of a 2.5 × 10^{-3} M solution of neopentyl isonitrile in benzene. The resulting solution was diluted to 25 mL with benzene, and the flask stoppered with a 10-mm rubber septum. After irradiation of the sample, 25 *μ*L of a 1.0 M solution of heptadecane in benzene was injected into the sample through the rubber septum. The mixture was thoroughly shaken to ensure homogeneity and then analyzed immediately by gas chromatography as described above.

X-ray Structural Studies of 2c,e and 3a. Similar procedures were used for all three complexes. Well-formed crystals of each compound were chosen from samples recrystallized from the solvents indicated in the preparations. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction with the program TRACER revealed primative crystal systems. Data were collected on the crystal in accord with the parameters in Table X. The space group was uniquely assigned on the basis of the systematic absences, and the correctness of this choice was confirmed by successful solution of the Patterson map, showing the rhodium atom. The Molecular Structure Corp. TEXSAN programs were used for solution and refinement of the structure.[27] Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for location of the hydrogen atoms, the coordinates of which were subsequently idealized. Final anisotropic refinement was carried out on all non-hydrogen atoms, with positional and thermal parameters of the hydrogens "riding" with the atom to which they were attached.

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Supplementary Material Available: Listings of anisotropic thermal parameters and bond distances and angles for RhCl(CNCH$_2$CMe$_3$)(P-*i*-Pr$_3$)$_2$, RhCl(CN-2,6-xylyl)(P-*i*-Pr$_3$)$_2$, and [Rh(CNCH$_2$CMe$_3$)$_2$(P-*i*-Pr$_3$)$_2$]Cl (30 pages); listings of calculated and observed structure factors for these compounds (51 pages). Ordering information is given on any current masthead page.

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(27) $R_1 = \{\sum||F_o| - |F_c||/\}\sum|F_o|\}$ and $R_2 = \{\sum w(|F_o| - |F_c|)^2\}^{1/2}/\{\sum wF_o^2\}$, where $w = \{\sigma^2(F_o) + [\rho F_o^2]^2\}^{1/2}$ for the non-Poisson contribution weighting scheme. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Source of scattering factors f_o, f', f'': Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B and 2.3.1.

Diastereotopic Group-Selective Reactions at π-Arene Chromium Derivatives: Deprotonation and Nucleophilic Addition Reactions of Substrates Bearing Benzylic Chiral Centers

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(η^6-(MeHXC)C$_6$H$_5$)Cr(CO)$_3$ (X = NMe$_2$ or OR) substrates undergo deprotonation by alkyllithium bases to produce, after quenching with electrophiles (E$^+$), high diastereomeric excesses (de) of (η^6-*o*-E-(MeHXC)C$_6$H$_4$)Cr(CO)$_3$ products. The *N*,*N*-dimethylamino substrate shows excellent chemoselectivity for ortho metalation, in addition to having ≥96% de in the formation of the product isomers. The propensity for ether derivatives to undergo benzylic deprotonation interferes with chemoselectivity in these substrates, although the selectivity for ortho substitution can be improved by employing chelating ether substituents and reduced reaction temperatures. The stereochemistry of deprotonation is evidently controlled by the tendency of the heteroatom side chain to adopt a conformation that minimizes steric interactions with the Cr(CO)$_3$ moiety and promotes the delivery of the ligated base to a specific ortho hydrogen. NOEDS studies indicate that the conformation of the benzylic side chain in the solutions containing only (η^6-(MeHXC)C$_6$H$_5$)Cr(CO)$_3$ probably closely mirrors those involved in the delivery of the alkyllithium reagent. Reactions between (η^6-(MeH(RO)C)C$_6$H$_5$)Cr(CO)$_3$ and *tert*-butyllithium in diethyl ether produced significant quantities of (η^4,η^2-2-*tert*-butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ after the mixture is quenched with a proton donor. The reaction displayed a peculiar temperature dependence, with an approximate 1:1 ratio of the *S**,*S**,*R** and *S**,*S**,*S** diastereomers being produced if the quench is performed below −40 °C and a 10:1 ratio of the *S**,*S**,*R** and *S**,*S**,*S** isomers, respectively, being produced by quenching the reaction at an ambient temperature. An X-ray crystallographic study unambiguously identified the molecule formed in predominance at elevated temperatures as the *S**,*S**,*R** *exo*-ethane *Z* isomer. Crystal data for (η^6-(*R**,*R**)-*o*-(Ph$_2$P)(MeH(Me$_2$N)C)C$_6$H$_4$)Cr(CO)$_3$ at 20 °C: a = 14.056 (4) Å, b = 9.730 (3) Å, c = 17.736 (5) Å, α = 105.78 (2)°, Z = 4, D_{calc} = 1.30, space group $P2_1/c$ and $R(F)$ = 0.044, $R_w(F)$ = 0.051 for 1434 reflections. Crystal data for (η^4,η^2-*S**,*S**,*R**-2-*tert*-butylcyclohexadienylidene-*exo*-ethane)Cr(CO)$_3$ at 23 °C: a = 13.457 (4) Å, b = 8.505 (2) Å, c = 14.350 (2) Å, α = 112.92 (2)°, Z = 4, D_{calc} = 1.31, space group $P2_1/c$ and $R(F)$ = 0.038, $R_w(F)$ = 0.050 for 1496 reflections.

Introduction

It is a matter of consensus that organometallic complexes play a major role in the development of new methodology in organic synthesis.[4] π-Arene chromium complexes have been particularly prominent in such endeavors, primarily due to the wide variety of useful organic molecules that can be obtained easily from modification

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(1) Department of Chemistry.

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(4) A variety of texts and monographs chronicle interest in these areas. For examples, see: (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987. (b) Davies, S. G. *Organotransition Metal Chemistry: Applications to Synthesis*; Pergamon Press: Oxford, 1982.

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