of the atomic parameters appear in Table II.

The cell parameters of powder samples of K_3TaS_4 and K_3TaSe_4 were each refined from 20 observations recorded at room temperature with an Enraf-Nonius FR552 Guinier camera ($\lambda(\mathrm{Cu}\ K\alpha_1) = 1.540562$ Å); Si SRM 640 ($a = 5.43088$ Å at 25 °C) was used as an internal standard. The cell constants are $a = 9.283$ (2), $b = 10.806$ (3), and $c = 9.387$ (2) Å for K_3TaS_4 and $a = 9.682$ (3), $b = 11.276$ (4), and $c = 9.712$ (3) Å for K_3TaSe_4.

Discussion

The structure of K_3NbS_4 is shown in Figure 1. It is built from the packing of NbS_4^{3-} anions and K^+ cations. Selected distances and angles are given in Table III. The Nb atom is tetrahedrally coordinated, and the range of Nb–S distances (from 2.241 (8) to 2.258 (8) Å) is near the sum of the ionic radii (2.32 Å).[16] The angles range from 108.3 (2) to 111.6 (3)° and are close to the tetrahedral value (109.47°). In K_3NbSe_4, the Nb–Se distances range from 2.387 (1) to 2.403 (1) Å and are also in fair agreement with the sum of the ionic radii (2.46 Å).[16] The Se–Nb–Se angles vary from 108.49 (3) to 111.68 (5)°. As expected, the metrical details of the $NbSe_4^{3-}$ ion are the same as those of the $TaSe_4^{3-}$ ion (Ta–Se = 2.369 (4)–2.397 (6) Å; Se–Ta–Se = 108.5 (2)–112.1 (2)°).[7]

The K–S geometries are not easily described in terms of classic polyhedra. If one takes a cutoff of 3.65 Å for the K–S distances, each K cation is surrounded by seven S atoms. The K–S distances range from 3.076 (10) to 3.604 (7) Å. Atom K(1) is linked to four different tetrahedra whereas atom K(2) is linked to five. A cutoff of 3.85 Å for the K–Se distances in K_3NbSe_4 leads to seven Se atoms about each K atom. The average value of 3.34 Å for the K–S distances and that of 3.48 Å for the K–Se distances are slightly longer than the sum of the ionic radii (3.30 and 3.44 Å, respectively). Similarly in Cs_3TaSe_4 the average Cs–Se distance is 3.71 Å compared with 3.70 Å for the sum of ionic radii. These compounds adopt orthorhombic symmetry and the interactions between the A cations and the Q atoms of the anions are essentially ionic, in accordance with the strong electronegativity difference ($\chi_S - \chi_K = 1.7$, $\chi_{Se} - \chi_K = 1.6$, and $\chi_{Se} - \chi_{Cs} = 1.7$). This is not true for Cu_3TaSe_4[5] and Tl_3TaSe_4[4] where the average A–Q distances are significantly shorter than the sums of ionic radii (Cu–Se = 2.41 Å versus 2.80 Å; Tl–Se = 3.22 Å versus 3.54 Å). If one considers the electronegativity differences ($\chi_{Se} - \chi_{Cu} = 0.5$ and $\chi_{Se} - \chi_{Tl} = 0.6$) between ions, then these interactions are much more covalent; this is evident in the shorter distances and perhaps in the more symmetric cubic structure. The weaker A–Q interactions observed in the alkali-metal tetrachalcogenometalates perhaps explain their solubility in nonaqueous solvents. The resultant solution chemistry is being investigated.

Acknowledgment. This research was supported by the National Science Foundation (Grant CHE-8701007).

Supplementary Material Available: Complete crystallographic details (Table IS), additional distances and angles (Table IIS), and anisotropic thermal parameters (Table IIIS) (4 pages); tables of observed and calculated structure amplitudes for K_3NbS_4 and K_3NbSe_4 (13 pages). Ordering information is given on any current masthead page.

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Preparation and Characterization of $(C_5Me_5)Rh(CNR)_2$ and $[(C_5Me_5)Rh(CNR)]_2$ Complexes

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Received May 19, 1989

Several complexes of the type $(C_5Me_5)M(CNR)X_2$ have been prepared, where M = Rh and Ir, X = Cl, Br, and I and R = Me, *t*-Bu, *neo*-Pn, *i*-Pr, 2,6-xylyl, and CH_2–adamantyl. Two members of this series have been structurally characterized. $(C_5Me_5)Rh(CNMe)Cl_2$ crystallizes in the monoclinic space group $P2_1/n$ with $a = 13.189$ (4) Å, $b = 8.442$ (2) Å, $c = 13.473$ (6) Å, $\beta = 111.31$ (6)°, $V = 1398$ (2) Å^3, and $Z = 4$. $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$ crystallizes in the monoclinic space group $P2_1/c$ with $a = 11.364$ (3) Å, $b = 8.436$ (3) Å, $c = 22.015$ (9) Å, $\beta = 97.33$ (3)°, $V = 2093$ (2) Å^3, and $Z = 4$. Reduction of the dihalide derivatives in the presence of isocyanide provides a general route to the bis-substituted products $(C_5Me_5)Rh(CNR)_2$ (R = Me, *t*-Bu, *neo*-Pn, *i*-Pr, 2,6-xylyl, CH_2–adamantyl). Reduction of the dihalide complexes in the absence of added isocyanide gives the dimers $[(C_5Me_5)Rh(\mu\text{-}CNR)]_2$, one of which has been characterized by X-ray crystallography (R = 2,6-xylyl). The molecule was found to crystallize in the monoclinic space group $P2_1/a$ with $a = 11.165$ (6) Å, $b = 13.222$ (5) Å, $c = 11.228$ (8) Å, $\beta = 98.43$ (5)°, $V = 1639.6$ (2.9) Å^3, and $Z = 4$.

Introduction

A wide variety of complexes of the general formula $CpML_2$ and $(C_5Me_5)ML_2$, where M = Co, Rh, and Ir, have been prepared and isolated over the past 20 years.[1-3] Some of these low-valent group 8 metals have shown activity toward C–H bonds, and our interest in low-valent isocyanide complexes led to the investigation of the complexes $(C_5Me_5)M(CNR)_2$.[4] These species have been observed in substitution reactions of $(C_5Me_5)M(CO)_2$ in solution[5] and in ligand-substitution reactions of $(\text{indenyl})Rh(C_2H_4)_2$.[6] Werner has recently reported the preparation of several $CpRh(CNR)_2$ complexes via $[RhCl(CNR)_2]_2$,[7] but a general preparation for the C_5Me_5 complexes has not appeared in the literature. In addition, while several μ-CO and μ-NO dimers of the type $[(C_5R_5)M(\mu\text{-}CO)_x(\mu\text{-}NO)_{2-x}]_2$ (R = H, Me; M = Co, Rh, Fe; x = 0, 1, 2) have been prepared[8] and structurally characterized,[9] only one isocyanide analogue has been reported, [CpNi-

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Table I. ^1H NMR and IR Spectral Data for the Complexes

complex	^1H NMR resonances,[a] δ C$_5$Me$_5$	CNR	IR (KBr), cm^{-1}
$(C_5Me_5)Rh(CNMe)_2$	2.211 (s)	2.441 (s, 6 H)	2110, 2044, 1959[c]
$(C_5Me_5)Rh(CN\text{-}i\text{-}Pr)_2$	2.200 (s)	3.40 (sept, J = 7 Hz, 2 H) 0.99 (d, J = 7 Hz, 12 H)	2080, 1969[d]
$(C_5Me_5)Rh(CN\text{-}t\text{-}Bu)_2$	2.179 (s)	1.127 (s, 18 H)	2055, 1910
$(C_5Me_5)Rh(CN\text{-}neo\text{-}Pn)_2$	2.234 (s)	2.803 (s, 18 H) 0.805 (d, J = 0.7 Hz, 4 H)	2073, 1977
$(C_5Me_5)Rh(CN\text{-}2,6\text{-}xylyl)_2$	2.189 (s)	2.259 (s, 12 H) 6.7 (m, 2 H) 6.5 (m, 4 H)	2017, 1979
$(C_5Me_5)Rh(CNCH_2Adm)_2$	2.262 (s)	2.781 (s, 4 H) 1.871 (br s, 6 H) 1.597 (d, J = 12 Hz, 6 H) 1.535 (d, J = 12 Hz, 6 H) 1.447 (d, J = 2.5 Hz, 12 H)	2075, 1990
$(C_5Me_5)Ir(CN\text{-}2,6\text{-}xylyl)_2$	1.74 (s)	2.31 (s, 12 H) 7.05 (m, 6 H)	
$(C_5Me_5)Rh(CNMe)Cl_2$[b]	1.692 (s)	3.544 (s, 3 H)	2212
$(C_5Me_5)Rh(CN\text{-}t\text{-}Bu)Cl_2$	1.761 (s)	1.553 (br s)	2202
$(C_5Me_5)Rh(CN\text{-}neo\text{-}Pn)Cl_2$	1.44 (s)	2.67 (s, 2 H) 0.73 (s, 9 H)	2221
$(C_5Me_5)Rh(CNMe)I_2$[b]	2.075 (s)	3.612 (s, 3 H)	2202
$(C_5Me_5)Rh(CN\text{-}neo\text{-}Pn)I_2$	1.78 (s)	2.58 (s, 2 H) 0.71 (s, 9 H)	2204
$(C_5Me_5)Rh(CN\text{-}2,6\text{-}xylyl)I_2$	1.76 (s)	2.26 (s, 6 H) 7.1 (m, 3 H)	2158
$(C_5Me_5)Ir(CN\text{-}neo\text{-}Pn)I_2$	1.73 (s)	2.82 (s, 2 H) 0.74 (s, 9 H)	2204
$(C_5Me_5)Ir(CN\text{-}2,6\text{-}xylyl)I_2$	1.74 (s)	2.31 (s, 6 H)	2140
$[(C_5Me_5)Rh(CN\text{-}neo\text{-}Pn)]_2$	1.663 (s)	1.259 (s, 18 H) 4.178 (s, 4 H)	1690[d]
$[(C_5Me_5)Rh(CN\text{-}2,6\text{-}xylyl]_2$	1.38 (s)	2.54 (s, 12 H) 7.0 (m, 6 H)	1707
$(C_5Me_5)Rh(CNCH_2CMe_3)(CO)$	2.04 (s)	2.50 (s, 2 H) 0.63 (s, 9 H)	2006, 1938
$(C_5Me_5)Rh(CN\text{-}2,6\text{-}xylyl)(CO)$	2.02 (s)	2.13 (s, 6 H) 6.7 (m, 3 H)	2001, 1923
$(C_5Me_5)Ir(CNCH_2CMe_3)(CO)$	2.03 (s)	2.73 (s, 2 H) 0.72 (s, 9 H)	2058, 1927
$(C_5Me_5)Ir(CN\text{-}2,6\text{-}xylyl)(CO)$	2.02 (s)	2.02 (s, 6 H) 7.0 (m, 3 H)	2063, 1919
$(C_5Me_5)Rh(CN\text{-}t\text{-}Bu)(PPh_3)$	1.946 (d, J = 0.9 Hz)	0.873 (s, 9 H) 7.025 (t, J = 7.1 Hz, 3 H) 7.096 (t, J = 6.8 Hz, 6 H) 7.795 (dd, J = 9.5, 8 Hz, 6 H)	2115
$(C_5Me_5)Rh(CN\text{-}t\text{-}Bu)(AsPh_3)$	1.996 (s)	0.909 (s, 9 H) 7.051 (t, J = 6.4 Hz, 3 H) 7.112 (t, J = 7.2 Hz, 6 H) 7.782 (t, J = 7.4 Hz, 6 H)	2105
$(C_5Me_5)Rh(CN\text{-}t\text{-}Bu)(SbPh_3)$	2.091 (s)	0.946 (s, 9 H) 7.131 (m, 9 H) 7.786 (d, J = 6.4 Hz, 6 H)	2115

[a] C_6D_6 solvent, 25 °C, except where noted. *neo*-Pn = neopentyl; Adm = adamantyl. [b] CD_2Cl_2 solvent. [c] Hexane solvent. [d] THF solvent.

$(CNMe)]_2$.[10] We report here on the preparation of both of these classes of complexes and provide several representative examples of their chemistry.

Results

A. Preparation of $(C_5Me_5)Rh(CNR)X_2$ Derivatives. The dichloro complexes are readily prepared by the reaction of the bridging chloride dimer $[(C_5Me_5)RhCl_2]_2$ with isocyanides. When a slurry of the dimer in THF is treated with 1 equiv of the isocyanide, the deep red complex is observed to go into solution as the orange isocyanide product is formed. Recrystallation from CH_2Cl_2/hexane gives large crystals of the product in >95% yield (eq 1). The complexes $(C_5Me_5)Rh(CNR)Cl_2$ and $CpRh(CNR)Cl_2$, where R = *t*-Bu or 2,6-xylyl, have been prepared earlier,[11] and the reaction of isocyanide with the dimer has been used as a means of assaying for small amounts of biologically significant isocyanide-containing compounds.[12]

$$[(C_5Me_5)RhCl_2]_2 + CNR \xrightarrow[THF]{} (C_5Me_5)Rh(CNR)Cl_2 \qquad (1)$$

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Table II. Summary of Crystallographic Data

	$(C_5Me_5)Rh(CNMe)Cl_2$	$(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$	$[(C_5Me_5)Rh(\mu\text{-}CN\text{-}2,6\text{-xylyl})]_2$
Crystal Parameters			
formula	$RhCl_2NC_{12}H_{18}$	$IrI_2NC_{19}H_{24}$	$RhNC_{19}H_{24}$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/a$
Z	4	4	4
a, Å	13.189 (4)	11.364 (3)	11.165 (6)
b, Å	8.442 (2)	8.436 (3)	13.222 (5)
c, Å	13.473 (6)	22.015 (9)	11.228 (8)
β, deg	111.31 (3)	97.33 (2.2)	98.43 (5)
vol, $Å^3$	1398 (2)	2093 (2)	1639.6 (2.9)
d_{calc}, g/cm^3	1.66	2.26	1.569
cryst dimens, mm	0.30 × 0.34 × 0.56	0.22 × 0.15 × 0.15	0.32 × 0.45 × 0.04
temp, °C	23	25	−75
Measurement of Intensity Data			
diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (graphite monochrom)	Mo (λ = 0.71073 Å)	Mo, (λ = 0.71073 Å)	Mo (λ = 0.71073 Å)
scan type	$2\theta/\omega$	$2\theta/\omega$	$2\theta/\omega$
scan rate, deg/min	2–16.5	2–16.5	1–16.5
total bkgd time	scan time/2	scan time/2	scan time/2
takeoff angle, deg	2.6	2.6	2.6
scan range, deg	$0.7 + 0.35 \tan \theta$	$0.8 + 0.35 \tan \theta$	$0.7 + 0.35 \tan \theta$
2θ range, deg	2–44	4–50	4–50
data collcd	$-h,-k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collcd	1855	3119	3177
no. of unique data $>3\sigma$	1601	2116	2076
no. of params varied	217	208	190
abs coeff, cm^{-1}	15.41	92.74	10.175
syst abs	$0k0$, k odd $h0l$, $h + l$ odd	$0k0$, k odd $h0l$, l odd	$0k0$, k odd $h0l$, h odd
abs cor	empirical	empirical	differential
range of transm factors	0.86–1.00	0.78–1.00	0.91–1.074
equiv data	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$	$0kl = 0k\bar{l}$
agreement between equiv data (F_o), %	0.3	3.0	0.5
R_1	0.027	0.034	0.050
R_2	0.042	0.044	0.059
goodness of fit	1.60	1.61	1.69

NMR spectral data for the complexes are summarized in Table I. Two features are worth noting about the spectra. First, while the free isocyanide ligand shows coupling between the α-hydrogens and the nitrogen (1:1:1 triplet), this coupling disappears upon complexation to the metal center, being replaced by only a broad resonance. Second, in the $^{13}C\{^1H\}$ NMR spectrum, the isocyanide carbon bound to the rhodium metal center couples not only to rhodium ($J \simeq 70$ Hz) but also to nitrogen ($J \simeq 20$ Hz). The long relaxation times of this quaternary carbon combined with the multiple couplings make this resonance difficult to observe.

The chloride complexes are readily converted into the bromide and iodide complexes by stirring a THF solution of the dichloride in the presence of a 10-fold excess of sodium halide. The solution of the complex is observed to darken as the substitutions occur. Alternatively, the dimer $[(C_5Me_5)RhI_2]_2$ can be used in the isocyanide-induced cleavage reaction. A few iridium dihalo isocyanide complexes were also prepared by this method.

The IR spectra of the complexes show the expected C≡N stretch in the region 2200–2220 cm^{-1}, consistent with bonding of the π-acceptor isocyanide ligand to a M(III) complex. Two of these complexes have been structurally characterized in order to ascertain the geometry of the CNR linkage.

The rhodium methyl isocyanide complex $(C_5Me_5)Rh(CNMe)Cl_2$ was crystallized by slow diffusion of hexane into a CH_2Cl_2 solution. Single-crystal X-ray examination in accord with the parameters given in Table II show the complex to exist with the anticipated tripod geometry around rhodium and with a nearly linear C–N–R linkage of 175.3° (Figure 1). The Rh–CNR bond length of 1.978 Å is slightly longer than that found in typical Rh–C double bonds (1.85–1.95 Å) and lies close to that observed in the carbene complex $(C_5Me_5)Rh[{=}C(tol)NHCH_2CMe_3]Cl_2$ (2.032 Å).[13]

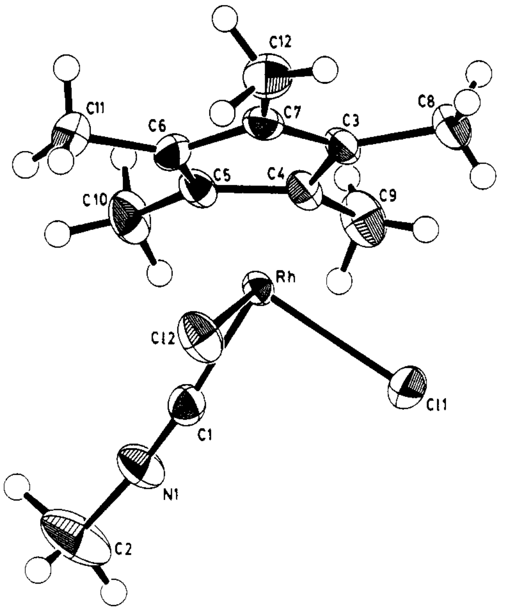

Figure 1. ORTEP diagram of $(C_5Me_5)Rh(CNMe)Cl_2$. Ellipsoids are shown at the 50% level.

Similarly, the iridium 2,6-xylyl isocyanide complex $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$ was structurally examined. It has a slightly bent isocyanide C–N–R linkage (166.3°) consistent with a slightly more electron-rich Ir(III) formulation (Figure 2). The Ir–C bond length of 1.930 Å is shorter than that seen in $(C_5Me_5)Ir(PMe_3)$(cyclohexyl)H (2.125 Å)[14] and $(C_5Me_5)Ir(PMe_3)$(vinyl)H (2.054)[15] consistent with a metal–carbon π-interaction. Other

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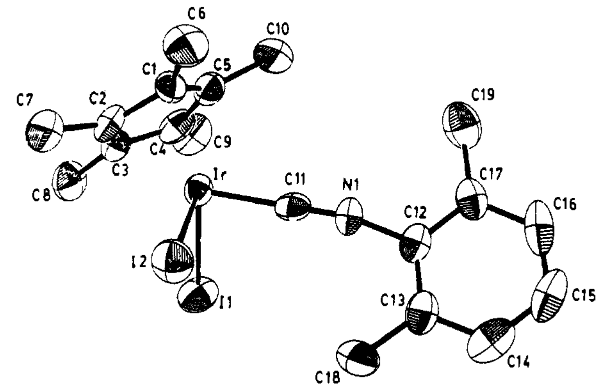


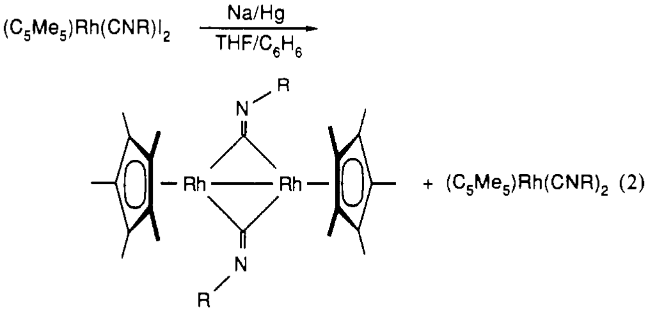
Figure 2. ORTEP diagram of $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$. Ellipsoids are shown at the 50% level.

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

	$(C_5Me_5)Rh(CNMe)Cl_2$		
	Bond Distances		
Rh1-Cl1	2.398 (1)	C1-N1	1.136 (6)
Rh1-Cl2	2.424 (1)	N1-C2	1.451 (7)
Rh1-C1	1.978 (5)		
	Bond Angles		
Cl1-Rh-Cl2	90.14 (5)	C1-N1-C2	175.3 (5)
Cl1-Rh-C1	92.1 (1)	Rh-C1-N1	173.8 (3)
Cl2-Rh-C1	88.6 (1)		
	$(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$		
	Bond Distances		
Ir-I1	2.704 (1)	C11-N1	1.133 (9)
Ir-I2	2.699 (1)	N1-C12	1.415 (10)
Ir-C11	1.930 (9)		
	Bond Angles		
I1-Ir-I2	93.41 (2)	C11-N1-C12	166.3 (9)
I1-Ir-C11	86.5 (2)	Ir-C11-N1	179.2 (7)
I2-Ir-C11	87.0 (2)		
	$[(C_5Me_5)Rh(\mu\text{-}CN\text{-}2,6\text{-xylyl})]_2$		
	Bond Distances		
Rh1-C11	1.967 (6)	C11-N1	1.234 (8)
Rh1-C11A	1.975 (6)	N1-C12	1.405 (9)
Rh1-Rh1A	2.556 (2)		
	Bond Angles		
C11-Rh1-C11A	99.1 (2)	Rh1-C11-N1	134.5 (5)
Rh1A-Rh1-C11	49.7 (2)	Rh1A-C11-N1	144.6 (5)
Rh1-C11-Rh1A	80.9 (2)	C11-N1-C12	140.9 (6)

relevant bond lengths and angles for these two complexes are given in Table III.

B. Reduction of $(C_5Me_5)Rh(CNR)X_2$ Derivatives. Reduction of $(C_5Me_5)Rh(CN\text{-}\mathit{neo}\text{-}Pn)I_2$ with 0.1% Na/Hg in 2:1 THF/C_6H_6 produced a dark olive green solution that contained two major rhodium containing complexes (eq 2). The major product



(2)

(80–90%) was isolated by repeated fractional crystallization of the reaction mixture from hexane. This complex was assigned the structure shown on the basis of spectroscopic evidence and by analogy to the 2,6-xylyl isocyanide derivative (vide infra). The ^1H NMR spectrum indicated a 1:1 ratio of C_5Me_5 and CNR ligands. The presence of equivalent bridging isocyanide ligands was established by ^{13}C NMR spectroscopy. A structurally similar complex $[(C_5Me_5Rh(CO)]_2$ has been reported by Nutton and Maitlis although the μ-CO ^{13}C NMR resonance was not observed.[16]

The second product in the above reduction was obtained in small yields (<10%) but was identified by comparison of its ^1H NMR, ^{13}C NMR, and IR spectral data with those of an independently prepared sample. The complex was prepared in virtually quantitative yield by the Na/Hg reduction of the rhodium diiodide complex in the presence of one equivalent of added neopentyl isocyanide (eq 3). The ^1H NMR spectrum exhibits a 1:2 ratio

$$(C_5Me_5)Rh(CNR)I_2 + CNR \xrightarrow[THF/C_6H_6]{Na/Hg} (C_5Me_5)Rh(CNR)_2 \qquad (3)$$

of C_5Me_5 to isocyanide ligands while the ^{13}C NMR (δ 166.92, d, $J = 82$ Hz) and IR (KBr: 2073 (s), 1977 (s) cm^{-1}) spectral data confirm the presence of two chemically equivalent terminal isocyanide ligands.

This methodology has also been used to prepare several complexes of the type $(C_5Me_5)M(L)(CNR)$, where L = CO, PPh_3, $AsPh_3$, or $SbPh_3$, by performing the reductions under an atmosphere of CO or in the presence of L. The reduction reaction can be accomplished with other reducing agents (i.e., sodium naphthalenide) and can also be used with the corresponding chloro and bromo complexes. However, the reduction of the diiodide complex is considerably faster and affords a much cleaner product mixture. Table I lists the isocyanide complexes that have been prepared by this technique and tabulates the NMR and IR spectral data.

It is important to note that mixed isocyanide complexes (i.e., $(C_5Me_5)Rh(CNR)(CNR')$) cannot be prepared in pure form by this technique. This is because traces of added isocyanide induce a rapid statistical scrambling of isocyanide ligands via an associative substitution process. This same bimolecular substitution process, which occurs quite rapidly in many $CpRhL_2$ complexes,[5b,17] will undoubtedly complicate the syntheses and study of other complexes using this method. The salient feature of this general technique is that it affords high yields of relatively pure products, although products with scrambled ligands can be anticipated if the second added ligand is likely to undergo associative substitution reactions.

C. Structure of $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$. The analogous dimeric xylyl isocyanide derivative $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$ has been prepared and structurally characterized. The molecule crystallizes in monoclinic space group $P2_1/a$ with the Rh–Rh axis lying on a crystallographic center of symmetry. Figure 3 shows an ORTEP plot of the molecule. The Rh–Rh distance of 2.556 Å can be compared with that of 2.564 Å in $[(C_5Me_5)Rh(CO)]_2$.[18] The isonitrile ligands are severely bent, with a C–N–C angle of 140.9. The complex $[(C_5Me_5)Co(CO)]_2$ has also been structurally characterized, although a two-site disorder of the C_5Me_5 groups was observed.[9h] Other complexes with μ-CNR ligands have been found or postulated to contain bent μ-CNR ligands.[10,19]

Discussion

Mechanism of Product Formation. The formation of the bis(isocyanide) complex and the bridging isocyanide dimer strongly suggest that the coordinatively unsaturated intermediate

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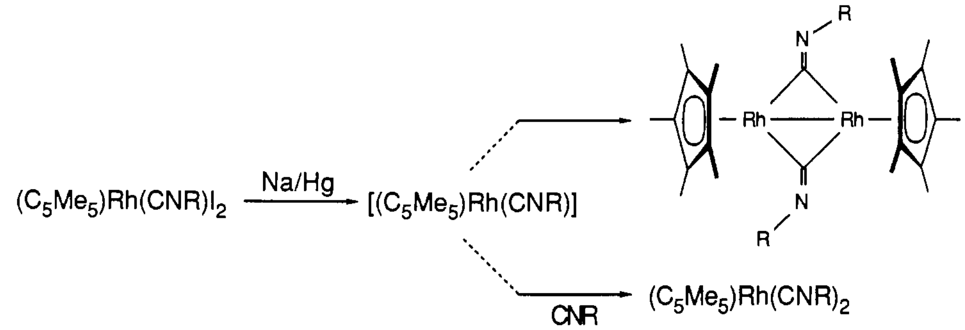
Scheme I



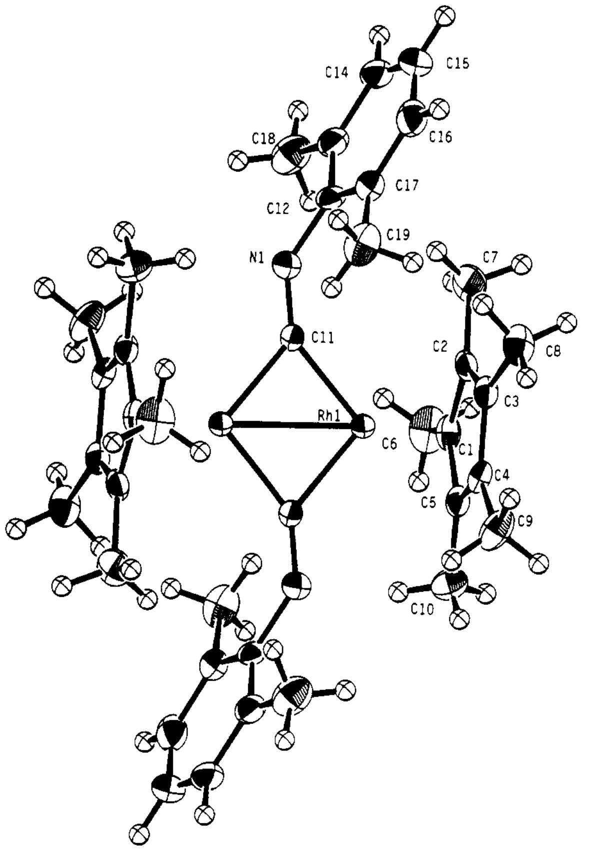


Figure 3. ORTEP diagram of $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$. Ellipsoids are shown at the 50% level.

$[(C_5Me_5)Rh(CNR)]$ was indeed formed (Scheme I) but that it was not capable of C–H activation of the benzene or THF solvent. It was initially believed that $[(C_5Me_5)Rh(CNR)]_2$ may have resulted from dimerization of this intermediate, while the bis(isocyanide) complex was due to isocyanide trapping of the intermediate.

The presence of bis(isocyanide) product in the reduction reaction to produce the dimer in the absence of added isocyanide was undoubtedly due to some decomposition reaction (e.g. overreduction) that produces free isocyanide. The observation of a peak assigned to $(C_5Me_5)Na$ in the ^1H NMR spectrum (δ 2.18) of the crude reaction mixture corroborates this suggestion. However, despite the simplicity in postulating the presence of the intermediate $[(C_5Me_5)Rh(CNR)]$ in these reactions, there is little direct evidence for the presence of such a species.

Several observations suggested that the bis(isocyanide) complex and the dimer were formed via reaction pathways that did not involve this species. First of all, and probably most importantly, reduction of the phosphine analogue $(C_5Me_5)Rh(PMe_3)I_2$ in THF/C_6H_6 also leads to a mixture of two complexes (currently unidentified) that contain (C_5Me_5) and PMe_3 as the only organic ligands. It does not produce $[(C_5Me_5)Rh(PMe_3)]$, which has been previously demonstrated to be very capable of both alkane and arene C–H bond activation.[20]

Second, the addition of olefins to the reduction mixtures has no noticeable effect. It would be expected that olefin trapping of the coordinatively unsaturated intermediate (rather than isocyanide trapping or dimerization) would yield olefin complexes such as $(C_5Me_5)Rh(CNR)(olefin)$, similar to the known $CpRh(CN\text{-}t\text{-}Bu)(C_2H_4)$ complex.[21] The lack of olefin complex formation by no means rules out that the bis(isocyanide) complex and the dimer are not formed as outlined in Scheme I. But when this observation is considered with information known about the analogous phosphine complexes (i.e. $(C_5Me_5)Rh(PMe_3)$), the intermediacy of $[(C_5Me_5)Rh(CNR)]$ seems highly improbable.

Third, independent photochemical studies with the bis(isocyanide) and mixed isocyanide/carbonyl derivatives leads to the formation of aldimine products via insertion of isocyanide into the aromatic C–H bonds of the solvent.[13] The functionalization reaction with $(C_5Me_5)Rh(CNR)(CO)$ is proposed to occur by way of the intermediate $[(C_5Me_5)Rh(CNR)]$. The present reduction experiments are therefore inconsistent with the intermediacy of $[(C_5Me_5)Rh(CNR)]$ on the basis of the behavior of the photochemical generated species.

It is likely that these reduction reactions proceed by way of odd-electron intermediates that can either undergo substitution or dimerization. In this fashion, the generation of coordinatively unsaturated 16-electron intermediates is avoided.

The complex $(C_5Me_5)Rh(CNCH_2CMe_3)_2$ is extremely stable toward thermolysis. A sealed NMR tube containing a C_6D_6 solution of $(C_5Me_5)Rh(CN\text{-}neo\text{-}Pn)_2$ was heated to 200 °C without any noticeable change. When the heating was continued for several additional hours or when the temperature was raised to 300 °C, the complex decomposed with the deposition of rhodium metal. Both ^1H NMR spectral data and GC analysis of the reaction mixture failed to detect any of the neopentylaldimine (or substantial quantities of any single organic compound) that might have resulted from benzene functionalization.

The bis(*tert*-butyl isocyanide) complex rapidly decomposed when heated to 100 °C in a sealed NMR tube containing C_6D_6. As with the neopentyl analogue, GC analysis failed to detect any benzaldimine, although large amounts of isobutylene were observed from dehydrocyanation of the coordinated *tert*-butyl isocyanide, an observation seen with other *tert*-butyl isocyanide complexes.[22]

Conclusions

A variety of cyclopentadienyl bis(isocyanide) and isocyanide carbonyl complexes can be prepared by way of reduction of the Rh(III) and Ir(III) dihalide complexes in the presence of a trapping ligand. Reductive coupling to form bis(μ-isocyanide) dimers occurs efficiently in the absence of added ligand. Reduction of the dihalide complexes does not appear to proceed through a 16-electron unsaturated intermediate.

Experimental Section

General Data. All solvents were distilled from dark purple solutions

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of sodium benzophenone ketyl under a nitrogen atmosphere. All compounds were handled in a Vacuum Atmospheres Dri-Lab drybox. All experiments were performed in sealed NMR tubes or ampules prepared and degassed on a high-vacuum line. Rhodium and iridium trichlorides were purchased from Johnson Matthey, Inc. *tert*-Butyl isocyanide and isopropyl isocyanide were purchased from Aldrich Chemical Co. 2,6-Xylyl isocyanide was purchased from Strem Chemical Co. Neopentyl isocyanide was synthesized as previously described.[22] The complexes $[(C_5Me_5)RhCl_2]_2$ and $[(C_5Me_5)RhI_2]_2$ were synthesized by using literature procedures.[23] Adamantylmethyl isocyanide was prepared by using the method of Ugi.[24]

NMR spectra were recorded on Bruker WH-400 and General Electric QE-300 NMR spectrometers. Electron-impact mass spectral analyses were conducted on a VG 7035 mass spectrometer at 20 or 70 eV. Elemental analyses were performed by Desert Analysis, Tuscon, AZ. Irradiations were carried out with an Oriel lamp housing and a 200-W high-pressure Hg focused-beam lamp. IR spectra were recorded on a Mattson Sirius 100 FTIR instrument. X-ray diffraction studies were carried out on an Enraf-Nonius CAD diffractometer.

Reaction of $[(C_5Me_5)RhCl_2]_2$ with Isocyanides. A 25-mL flask containing 179 mg (0.29 mmol) of $[(C_5Me_5)RhCl_2]_2$ was attached to the vacuum line and cooled to 77 K and THF (15 mL) distilled in (25 °C, 10^{-3} mm). Methyl isocyanide was then measured out as a gas on the vacuum line (128 mm, 86.5 mL, 295 K) and condensed into the flask. The slurry was stirred for 30 min (during which period the red solid took on an orange-red color) and then evaporated to dryness. The product was taken up in 5 mL of CH_2Cl_2 (in air) and the solution layered with hexane (10 mL). Large red crystals of $(C_5Me_5)Rh(CNMe)Cl_2$ grew over several days. Yield: 197 mg (97%). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 9.233 (s, $C_5\mathit{Me}_5$), 30.991 (s, $CN\mathit{CH}_3$), 99.765 (d, J = 7.0 Hz, C_5Me_5), 136.314 (dt, J = 69.3, 20.0 Hz, $\mathit{C}NCH_3$). Anal Calcd (found) for $RhNCl_2C_{12}H_{18}$: C, 41.17 (41.20); H, 5.18 (5.22); 4.00 (3.90). IR (KBr): 2212 cm^{-1}. Complexes with isopropyl, *tert*-butyl, neopentyl, 2,6-xylyl, and adamantylmethyl isocyanide were prepared similarly.

Halide Metathesis Reactions. The preparation is detailed by using the methyl isocyanide complex as an example. $(C_5Me_5)Rh(CNMe)Cl_2$ (150 mg, 0.39 mmol) and NaI (646 mg, 3.9 mmol) were dissolved in acetone (15 mL) and refluxed for $^1/_2$ h. The solvent was removed under vacuum and the product taken up in CH_2Cl_2 (10 mL) and filtered. The residual KI was washed with CH_2Cl_2 (3 × 5 mL) and the combined washings concentrated to ~5 mL and layered with hexane (15 mL). Large crystals of the red-purple diiodide product separated and were collected by filtration. Yield: 212 mg (100%). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 11.165 (s, $C_5\mathit{Me}_5$), 31.063 (s, $CN\mathit{CH}_3$), 100.843 (d, J = 21.3 Hz, C_5Me_5), 132.333 (dt, J = 68, 13 Hz, $\mathit{C}NCH_3$). Anal Calcd (found) for $RhNI_2C_{12}H_{18}$: C, 27.04 (27.18); H, 3.40 (3.39); N, 2.63 (2.51). IR-(KBr): 2202 cm^{-1}.

Reduction of $(C_5Me_5)Rh(CNR)I_2$ in the Presence of Added L. The procedure is described for the bis(neopentyl isocyanide) complex. Sodium amalgam (10.8 g of 0.47% Na/Hg, 2.2 mmol) was added to a solution of $[(C_5Me_5)RhI_2]_2$ (490 mg, 0.5 mmol) and neopentyl isocyanide (265 μL, 2.2 mmol) in THF (10 mL). (The latter two compounds form a solution of $(C_5Me_5)Rh(CNR)I_2$ in situ.) The reaction mixture was stirred until the solution turned bright orange (20 min), and the solution was then decanted and evaporated (25 °C, 10^{-3} mm). The residue was extracted with hexane (20 mL), the extract filtered through a fine sintered-glass funnel, and the filtrate evaporated (25 °C, 10^{-3} mm) to give 424 mg (98%) of $(C_5Me_5)Rh(CNCH_2CMe_3)_2$ as a bright orange microcrystalline solid. The compound is very air-sensitive and very soluble in most organic solvents. ^{13}C NMR ($CDCl_3$): δ 11.84 (q, J = 125 Hz), 26.73 (q, J = 127 Hz), 32.24 (s), 56.51 (t, J = 128 Hz), 97.66 (s), 166.92 (d, J = 82 Hz). IR (KBr): 2073, 1977 cm^{-1}. MS (75 eV): *m/e* 432 (M^+). UV (C_6H_{12}): λ_{max} 350 nm (ϵ 7250), 246 nm (ϵ 20 900).

The above procedure was used to prepare a variety of other bis(isocyanide) complexes from $[(C_5Me_5)RhI_2]_2$ and the appropriate isocyanide. The bis(methyl isocyanide) complex required extraction with toluene rather than hexane. For $(C_5Me_5)Rh(CNMe)_2$, $^{13}C\{^1H\}$ (CD_2Cl_2): δ 10.670 (s), 32.318 (s), 100.919 (d, J = 4.5 Hz), 141.119 (d, J = 67.9 Hz). Several mono(isocyanide)–Rh(I) complexes were prepared from the reduction of $(C_5Me_5)Rh(CNR)I_2$ in the presence of other coordinating ligands (CO, PPh_3, $AsPh_3$, $SbPb_3$) as summarized in Table I.

Preparation of $[(C_5Me_5)Rh(CNCH_2CMe_3)]_2$. Sodium amalgam (3.0 g of 0.1% Na/Hg, 0.13 mmol) was added to a solution of $(C_5Me_5)Rh(CNCH_2CMe_3)I_2$ (35 mg, 0.059 mmol) in 5 mL of THF/C_6H_6 (2:1). The reaction mixture was stirred for 15 min at 25 °C, and the dark olive solution was then decanted and evaporated (25 °C, 10^{-3} mm). Repeated fractional crystallization of the residue from hexane afforded a dark blue microcrystalline compound, which was identified as $[(C_5Me_5)Rh(CNCH_2CMe_3)]_2$ on the basis of ^1H NMR, ^{13}C NMR, and IR spectral data. The dimer constituted ~80% of the crude reduction mixture as determined by ^1H NMR spectroscopy. Approximately 10% of the bis(isocyanide) complex $(C_5Me_5)Rh(CNCH_2CMe_3)_2$ was also identified. For $[(C_5Me_5)Rh(CNCH_2CMe_3)]_2$, ^{13}C NMR($CDCl_3$): δ 11.31 (q, J = 126 Hz), 28.31 (q, J = 127 Hz), 32.73 (s), 68.70 (t, J = 128 Hz), 100.14 (s), 234.95 (t, J = 53 Hz). IR (THF): 1690 cm^{-1}. The bis(xylyl isocyanide) dimer was prepared in an analogous fashion.

Table IV. Positional Parameters for $(C_5Me_5)Rh(CNMe)Cl_2$

atom	*x*	*y*	*z*
Rh	0.53391 (2)	0.31949 (3)	0.28542 (2)
Cl1	0.35456 (7)	0.4289 (1)	0.20663 (8)
Cl2	0.60945 (8)	0.5841 (1)	0.32371 (8)
N1	0.5766 (3)	0.3206 (4)	0.0731 (3)
C1	0.5572 (3)	0.3275 (4)	0.1486 (4)
C2	0.6087 (8)	0.3036 (8)	−0.0185 (6)
C3	0.4905 (3)	0.1755 (4)	0.4025 (3)
C4	0.4966 (3)	0.0813 (4)	0.3157 (3)
C5	0.6073 (3)	0.0886 (4)	0.3204 (3)
C6	0.6646 (3)	0.1954 (4)	0.4022 (3)
C7	0.5911 (3)	0.2467 (4)	0.4555 (3)
C8	0.3904 (4)	0.1905 (6)	0.4301 (5)
C9	0.4092 (4)	−0.0221 (7)	0.2435 (4)
C10	0.6517 (4)	−0.0057 (6)	0.2514 (4)
C11	0.7819 (3)	0.2390 (7)	0.4381 (5)
C12	0.6221 (4)	0.3519 (6)	0.5497 (4)

Table V. Positional Parameters for $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$

atom	*x*	*y*	*z*
Ir	0.66356 (3)	0.59545 (5)	0.64162 (2)
I1	0.82562 (7)	0.8078 (1)	0.69203 (4)
I2	0.51777 (7)	0.82155 (9)	0.58785 (4)
N1	0.7916 (6)	0.608 (1)	0.5275 (3)
C1	0.5388 (8)	0.398 (1)	0.6377 (4)
C2	0.5184 (8)	0.492 (1)	0.6897 (4)
C3	0.6223 (9)	0.497 (1)	0.7312 (4)
C4	0.7142 (9)	0.404 (1)	0.7061 (5)
C5	0.6573 (8)	0.339 (1)	0.6488 (4)
C6	0.4460 (9)	0.357 (1)	0.5848 (5)
C7	0.402 (1)	0.566 (2)	0.7005 (6)
C8	0.644 (1)	0.577 (2)	0.7928 (5)
C9	0.830 (1)	0.366 (2)	0.7401 (5)
C10	0.715 (1)	0.228 (1)	0.6079 (6)
C11	0.7450 (8)	0.604 (1)	0.5699 (5)
C12	0.8428 (7)	0.652 (1)	0.4746 (4)
C13	0.8553 (8)	0.812 (1)	0.4633 (5)
C14	0.9044 (9)	0.851 (1)	0.4113 (5)
C15	0.937 (1)	0.734 (2)	0.3733 (5)
C16	0.9252 (9)	0.580 (2)	0.3856 (5)
C17	0.8750 (8)	0.532 (1)	0.4371 (4)
C18	0.814 (1)	0.935 (1)	0.5043 (6)
C19	0.8549 (9)	0.359 (1)	0.4497 (5)

X-ray Structural Determination of $(C_5Me_5)Rh(CNMe)Cl_2$. Well-formed orange crystals of the compound were prepared by slow diffusion of hexane into a CH_2Cl_2 solution. The lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Cell reduction with the program TRACER revealed a primative monoclinic crystal system. Data were collected on the crystal in accord with the parameters in Table II. The space group was uniquely assigned as $P2_1/n$ on the basis of the systematic absences (0*k*0, *k* odd; *h*0*l*, *h* + *l* odd). 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.[25] Anisotropic refinement of all non-hydrogen atoms allowed the use of a difference Fourier map for location of the hydrogen atoms. Final anisotropic refinement was carried out on all 16 non-hydrogen atoms, with both positional and thermal parameters of the hydrogens

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(24) Ugi, I.; Meyr, R. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. 5, p 1060.

(25) $R_1 = \{\sum||F_o| - |F_c||\}/\{\sum|F_o|\}$; $R_2 = \{\Sigma w(|F_o| - |F_c|)^2\}^{1/2}\{\Sigma wF_o^2\}$; 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', and f'': Cromer, D. T.; Waber, J. T. *International Tables for X-Ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2B and 2.3.1.

Table VI. Positional Parameters for $[(C_5Me_5)Rh(m\text{-}CN\text{-}2,6\text{-xylyl})]_2$

atom	*x*	*y*	*z*
Rh1	0.44175 (4)	0.03882 (4)	0.07860 (4)
N1	0.3333 (5)	0.0869 (5)	−0.1721 (5)
C1	0.4170 (6)	0.1758 (5)	0.1905 (6)
C2	0.4372 (6)	0.0900 (6)	0.2687 (6)
C3	0.3415 (6)	0.0213 (5)	0.2352 (6)
C4	0.2616 (6)	0.0650 (5)	0.1350 (6)
C5	0.3085 (6)	0.1611 (5)	0.1101 (6)
C6	0.4953 (8)	0.2688 (6)	0.2011 (8)
C7	0.5357 (7)	0.0799 (7)	0.3723 (7)
C8	0.3150 (7)	−0.0727 (6)	0.3004 (8)
C9	0.1482 (7)	0.0182 (6)	0.0727 (8)
C10	0.2513 (8)	0.2361 (7)	0.0188 (8)
C11	0.4117 (5)	0.0468 (5)	−0.0982 (5)
C12	0.3161 (6)	0.1263 (5)	−0.2896 (6)
C13	0.2228 (7)	0.0862 (6)	−0.3724 (7)
C14	0.2047 (7)	0.1272 (8)	−0.4878 (7)
C15	0.2756 (8)	0.2041 (8)	−0.5190 (7)
C16	0.3664 (8)	0.2429 (7)	−0.4348 (8)
C17	0.3887 (7)	0.2062 (6)	−0.3194 (6)
C18	0.1456 (8)	0.0028 (7)	−0.3384 (8)
C19	0.4835 (8)	0.2528 (7)	−0.2265 (8)

being refined. Table III contains relevant bond distances and angles, and Table IV contains positional parameters.

X-ray Structural Determination of $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$. Well-formed orange crystals of the compound were prepared by slow evaporation from a CH_2Cl_2 solution. The data collection and reduction were carried out as described above for the rhodium commplex with the parameters given in Table II. Systematic absences uniquely indicated the space group as $P2_1/c$. The structure was solved by using standard heavy-atom methods. Hydrogen atoms were placed in locations based upon peaks in the difference Fourier map but were not varied in the final refinement. Table III contains relevant bond distances and angles, and Table V contains positional parameters.

X-ray Structural Determination of $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$. A small well-formed dark green plate of the compound was prepared by slow evaporation of a hexane solution, mounted to a glass fiber, and coated with epoxy. The sample was cooled to −75 °C in a nitrogen stream, and the lattice constants were obtained from 25 centered reflections with values of χ between 10 and 60°. Initial indexing produced a monoclinic cell. While cell reduction with the program TRACER revealed a centered orthorhombic crystal system (90° ± 0.4°), axial photographs in this setting did not show the required Laue symmetry, but rather were consistent with a monoclinic system. Consequently, data were collected on the crystal in the monoclinic setting in accord with the parameters given in Table II. The space group was assigned as $P2_1/a$ on the basis of the systematic absences. A Patterson map solution showed a Rh atom near a center of symmetry that generated the second half of the dimer, giving a total of two molecules (four halves) per unit cell. Structure expansion with the program DIRDIF revealed all other non-hydrogen atoms. Following isotropic refinement, the program DIFABS was employed to correct for absorption. Full anisotropic refinement with placement of the hydrogen atoms in idealized positions based upon peaks in the difference Fourier map yielded the final structure shown in Figure 3. We thank a reviewer for encouraging us to reexamine the initial orthorhombic cell (which produced an incorrect disordered solution) during review of this manuscript. Table III contains relevant bond distances and angles, and Table VI contains positional parameters.

Acknowledgment is made to the U.S. Department of Energy (Grant DE-FG02-86ER13569) for their partial support of this work. W.D.J. also thanks the Alfred P. Sloan and Camille and Henry Dreyfus Foundations for awards.

Supplementary Material Available: Listings for $(C_5Me_5)Rh(CNMe)Cl_2$, $(C_5Me_5)Ir(CN\text{-}2,6\text{-xylyl})I_2$, and $[(C_5Me_5)Rh(CN\text{-}2,6\text{-xylyl})]_2$ of anisotropic thermal parameters, bond distances and angles, and hydrogen atom parameters (17 pages); listings for all these compounds of calculated and observed structure factors (49 pages). Ordering information is given on any current masthead page.

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Reaction of $ReH_7(PPh_3)_2$ with Silanes: Preparation and Characterization of the First Silyl Polyhydride Complexes, $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$, $SiEt_3$, $SiHEt_2$)

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Received June 26, 1989

Reaction of silanes with $ReH_7(PPh_3)_2$ (**1**) gives the novel rhenium silyl hexahydride complexes $ReH_6(SiR_3)(PPh_3)_2$ (SiR_3 = $SiPh_3$ (**2a**), $SiEt_3$ (**2b**), $SiHEt_2$ (**2c**)), which have been fully characterized by IR and ^1H, ^{31}P, and ^{13}C NMR spectroscopy and, in the case of **2a**, by single-crystal X-ray crystallography. The spectroscopic and X-ray diffraction data suggest that **2a–c** probably have a classical nine-coordinate tricapped trigonal-prismatic structure with the two phosphine ligands and the silyl group occupying the three equatorial sites and the six hydride ligands occupying the six axial positions. **2a** has been obtained in two crystalline forms, one solvated (CH_2Cl_2) and the other unsolvated, and structures were determined on both. Crystals of the unsolvated **2a** belong to space group $P\bar{1}$ with a = 9.293 (3) Å, b = 13.037 (3) Å, c = 19.152 (2) Å, α = 86.50 (1)°, β = 88.83 (2)°, γ = 88.40 (2)°, V = 2315 (2) Å^3, Z = 2, and ρ_{calcd} = 1.401 (1) g/cm^3. Crystals of **2a**·CH_2Cl_2 belong to space group $P2_1/c$ with a = 10.416 (1) Å, b = 24.065 (5) Å, c = 19.505 (3) Å, β = 100.16 (1)°, V = 4812 (1) Å^3, Z = 4, and ρ_{calcd} = 1.463 (1) g/cm^3. The Re–Si bond lengths, 2.474 (4) Å (**2a**) and 2.475 (4) Å (**2a**·CH_2Cl_2), are shorter than the sum of the covalent radii of the Re and Si atoms (2.65 Å), which is unusual for a transition-metal silyl complex with a formal d^0 configuration.

Introduction

The synthesis and structural characterization of transition-metal polyhydride complexes are of current interest.[1] Many of these complexes undergo a variety of catalytic and stoichiometric reactions, including alkane conversion. This seems to be a result of their ability to generate reactive intermediate species containing vacant coordination sites by elimination of H_2 through thermolysis, photolysis, or acidolysis. Very recently, some polyhydride complexes have been reformulated as having a nonclassical structure containing η^2-H_2 ligands bound in a molecular fashion.[2] The presence of these η^2-H_2 ligands may be related to the facile loss of H_2 found in some cases.

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