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Reactions of Isocyanides with Rhodium Porphyrins: Formation of Formimidoyl and Carbamoyl Complexes and CN–R Bond Cleavage

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Reactions of alkyl and aryl isocyanides with (octaethylporphyrinato)rhodium hydride, (OEP)Rh—H, (octaethylporphyrinato)rhodium(II) dimer, $[(OEP)Rh]_2$, and (tetramesitylporphyrinato)rhodium(II), (TMP)Rh•, have been investigated for comparison with CO reactivity. Alkyl and aryl isocyanides interact with (OEP)Rh—H to form 1:1 adducts, (OEP)Rh(H)(CNR), which react further to produce formimidoyl complexes, (OEP)Rh—CH=NR, in analogy with the reaction of (OEP)Rh—H with CO that produces a formyl complex, (OEP)Rh—CHO. $[(OEP)Rh]_2$ forms 1:1 complexes with isocyanides where the 2,6-dimethylphenyl isocyanide derivative persists at equilibrium, but alkyl isocyanides undergo CN— alkyl bond cleavage to form alkyl, (OEP)Rh—R, and cyanide, (OEP)Rh(CN)(CNR), complexes. No evidence was obtained for bridging isocyanide species analogous to the dimetal ketone RhC(O)Rh and dimetal diketone RhC(O)C(O)Rh complexes observed in reactions of $[(OEP)Rh]_2$ with CO. Carbamoyl complexes, (OEP)Rh— C(O)NHR, are formed in reactions of $[(OEP)Rh]_2$ with CNR and H_2O or CO and RNH_2. The crystal and molecular structures were determined for (OEP)Rh—C(O)NH($C_6H_3(CH_3)_2$) which crystallizes in the triclinic space group $P\bar{1}$ with unit cell dimensions $a = 12.256(3)$ Å, $b = 13.234(2)$ Å, $c = 15.075(3)$ Å, $\alpha = 61.79(2)°$, $\beta = 75.89(2)°$, $\gamma = 73.39(1)°$, $V = 2047.7(7)$ Å^3, and $Z = 2$.

Introduction

Binding of carbon monoxide by rhodium(III) and rhodium(II) porphyrin species has been shown to activate CO toward conventional reactions with nucleophiles and unusual radical-like reactions at the carbonyl carbon.[1,2] Metallo radical—CO complexes, $[(por)RhCO]^•$, have been implicated in acyl radical-like reactions that reduce CO and produce complexes containing formyl (HC(O)–)[3–5] or ketone (–C(O)–)[6–8] units. Alkyl and aryl isocyanide ligands (:C≡N—R) are electronically related to carbon monoxide (:C≡O) and their coordination chemistry and ligand reactions are often closely related.[9] Cationic isocyanide complexes of (octaethylporphyrinato)rhodium(III), $[(OEP)Rh(CNR)_2]^+$, have previously been shown to react with nucleophiles to form cationic carbenes, neutral carbamoyl, and metalloester species.[10] This article is focused on a comparative study of solution reactions of isocyanides and carbon monoxide with (OEP)Rh—H, $[(OEP)Rh]_2$, and (tetramesitylporphyrinato)rhodium(II), (TMP)Rh•.

Results

Reactions of Isocyanides with Rhodium(II) Porphyrins. $[(OEP)Rh]_2$. Benzene solutions of $[(OEP)Rh]_2$ ($\sim 10^{-3}$ M) interact with methyl and *n*-butyl isocyanides ($\sim 10^{-2}$ M) to form 1:1 isocyanide adducts. A subsequent slower reaction cleaves the CN—R bond, producing equal quantities of alkyl and cyanide complexes (eqs 1 and 2)

$$[(OEP)Rh]_2 + CNR \rightleftharpoons [(OEP)Rh]_2CNR \quad (1)$$

$$[(OEP)Rh]_2 + 2CNR \rightleftharpoons (OEP)Rh{-}R + (OEP)Rh(CN)(RNC) \quad (2)$$

(Figure 1). The cyanide complex contains a coordinated isocyanide ligand that is observed by the high field ^1H NMR resonances of the coordinated alkyl isocyanide group (Figure 1). The alkyl complex also coordinates an isocyanide ligand to form (OEP)Rh(R)(RNC), as evidenced by the high field shifts of the Rh—R alkyl resonances from their positions in the five-coordinate complexes ((OEP)Rh—R), but in this case the coordinated isocyanide is in fast exchange with excess free ligand in solution. Removal of solvent and excess free ligand under vacuum and subsequent dissolution in C_6D_6 results in observation of a five-coordinate alkyl complex, (OEP)Rh—R, and a six-coordinate cyanide complex, (OEP)Rh(CN)(RNC), which were identified by comparison with samples of the compounds prepared by independent synthesis. Infrared spectra of (OEP)Rh(CN)(RNC) complexes show two CN bands ($\nu_{C≡N}$ = 2235–2195 cm^{-1} and $\nu_{C≡N}$ = 2135–2131 cm^{-1}) corresponding to the coordinated isocyanides and to the cyanide ligands, respectively.

Using an aryl isocyanide (2,6-dimethylphenyl isocyanide) eliminates the R–NC bond cleavage reaction and thus provides a convenient system for investigating

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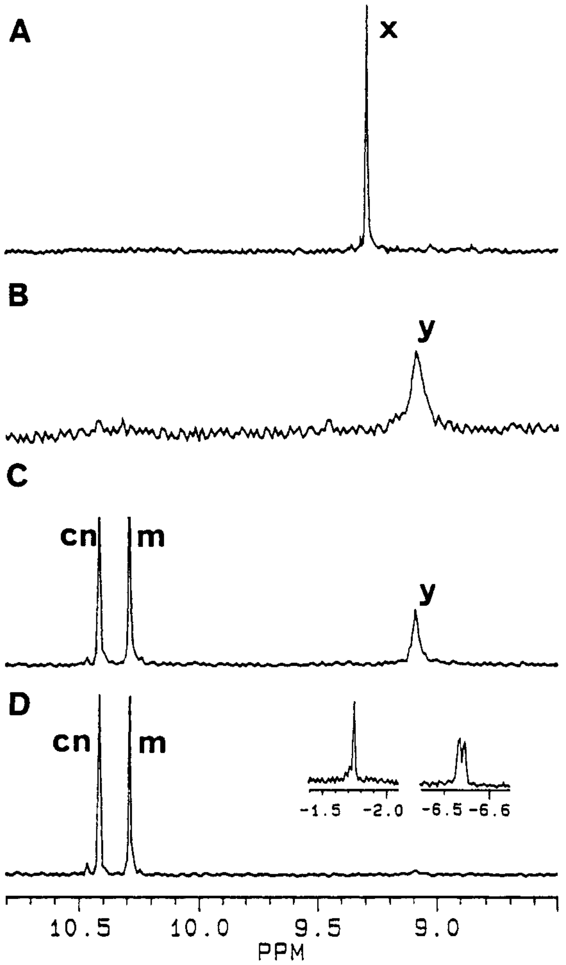


Figure 1. ^1H NMR (200-MHz) spectra for the porphyrin methine resonances for a solution of $[(OEP)Rh]_2$ with CH_3NC (at 298 K; in C_6D_6): (A) $[(OEP)Rh]_2$; (B) 2 min after CH_3NC addition; (C) after 40 min; (D) completed reaction (100 min). ((cn) $(OEP)Rh(CN)(CH_3NC)$; (m) $(OEP)Rh(CH_3)(CH_3NC)$; (x) $[(OEP)Rh]_2$; (y) $[(OEP)Rh]_2(CH_3NC)$.)

isocyanide complex formation with $[(OEP)Rh]_2$ without complicating additional reactions. When less than a stoichiometric quantity of 2,6-dimethylphenyl isocyanide is mixed with $[(OEP)Rh]_2$, two sets of porphyrin ^1H NMR resonances are observed for $[(OEP)Rh]_2CNR$, indicating coordination of CNR to one Rh site and slow exchange of CNR between the two rhodium sites in $[(OEP)Rh]_2$ (Figure 2). This is most clearly illustrated in the ^1H NMR spectrum in toluene-d_8 at 208 K where the methine resonance for $[(OEP)Rh]_2$ is resolved from the two methine resonances associated with $[(OEP)Rh]_2CNR$ (Figure 2C). Presence of the isocyanide ligand in excess of 1:1 stoichiometry results in averaging of the ^1H NMR positions for the inequivalent (OEP)Rh units in $[(OEP)Rh]_2CNR$, indicating fast ligand exchange between the 1:1 complex and free isocyanide even at −65 °C. Mole ratios of isocyanide to $[(OEP)Rh]_2$ of up to 30 do not result in shifting of the (OEP)Rh ^1H NMR resonances from the averaged positions of the 1:1 complex, suggesting that relatively little 2:1 complex is present under the range of concentrations studied. Parallel studies of methyl and *n*-butyl isocyanide with $[(OEP)Rh]_2$ also gave results compatible with exclusive 1:1 complex formation.

(TMP)Rh^{II}. Toluene solutions containing $(TMP)Rh^\bullet$ ($\sim 10^{-3}$ M) when mixed with 2,6-dimethylphenyl isocyanide ($\sim 10^{-2}$ M) at low temperature (200 K) and then frozen (90 K) exhibit the EPR spectrum illustrated in Figure 3. The observed g values ($g_\perp = 2.158, g_\parallel = 1.995$) are consistent with a primarily rhodium based odd electron occupying a d_{z^2} molecular orbital (mo).[1] Ligand hyperfine splitting on the g_3 transition from the isocyanide nitrogen demonstrates that the species present is a 1:1 complex, $[(TMP)Rh(CNR)]^\bullet$.

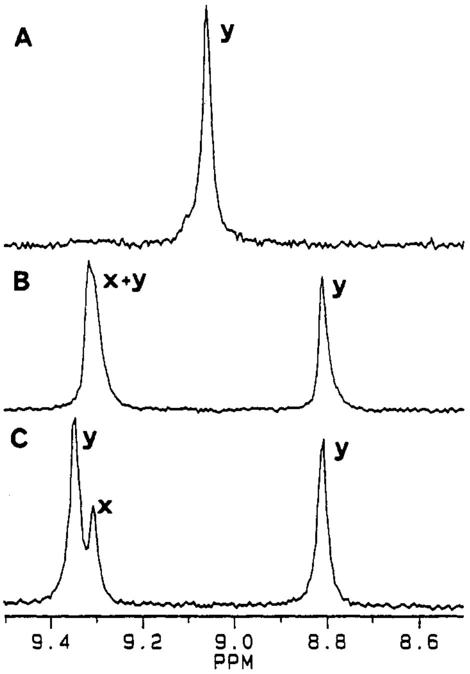


Figure 2. ^1H NMR (200-MHz) spectra for the porphyrin methine resonances for $[(OEP)Rh]_2(C_6H_3(CH_3)_2NC)$ in toluene-d_8: (A) excess isocyanide (298 K); (B) excess $[(OEP)Rh]_2$ (298 K); (C) excess $[(OEP)Rh]_2$ (208 K). ((x) $[(OEP)Rh]_2$; (y) $[(OEP)Rh]_2(C_6H_3(CH_3)_2NC)$.)

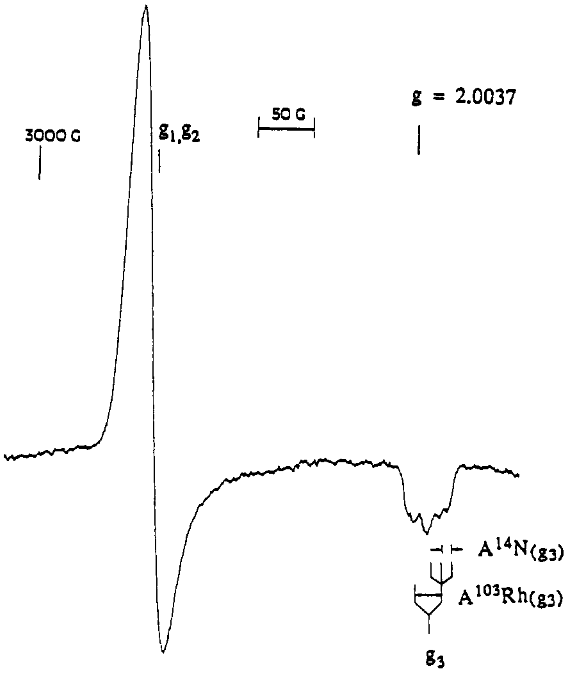


Figure 3. Anisotropic EPR spectrum for $[(TMP)Rh(C_6H_3(CH_3)_2NC)]^\bullet$ in toluene at 90 K ($g_1 \sim g_2 \sim 2.158$, $g_3 = 1.995$, $A(^{103}Rh) = 60$ MHz, $A(^{14}N) = 28$ MHz).

Mixing benzene solutions of $(TMP)Rh^\bullet$ ($\sim 10^{-3}$ M) with CH_3NC ($\sim 10^{-2}$ M; T = 295 K) results in quantitative formation of equal amounts of cyanide and methyl

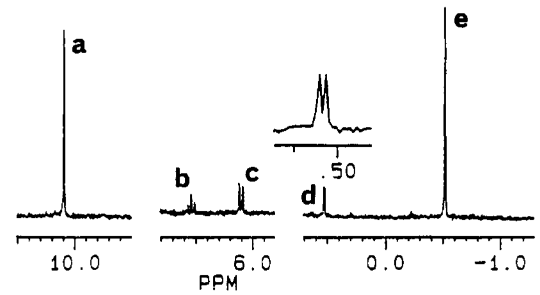


Figure 4. ^{1}H NMR (200-MHz) spectrum of (OEP)-Rh—CH=N($C_6H_3(CH_3)_2$) formed in the reaction of (OEP)Rh—H and 2,6-dimethylphenyl isocyanide (298 K in C_6D_6) (a) porphyrin methine; (b) aryl *p*-H; (c) aryl *m*-H; (d) Rh—CH=; (e) 2,6-dimethylphenyl methyls).

derivatives during the time required to record the ^{1}H NMR spectrum (eq 3). $(\mathrm{TMP})\mathrm{Rh}^\bullet$ similarly reacts with *n*-BuNC

$$2(\mathrm{TMP})\mathrm{Rh}^\bullet + 2\mathrm{CNCH_3} \xrightarrow{\mathrm{C_6D_6}} (\mathrm{TMP})\mathrm{Rh\text{-}CH_3} + (\mathrm{TMP})\mathrm{Rh(CN)(CH_3NC)} \tag{3}$$

to form *n*-butyl and cyanide derivatives quantitatively; however the *n*-BuNC reaction is substantially slower than that observed for CH_3NC.

Reactions of Isocyanides with (OEP)Rh-H. Benzene solutions of (OEP)Rh-H ($\sim 10^{-3}$ M) initially react with alkyl and aryl isocyanides ($\sim 10^{-2}$ M) to form 1:1 adducts (eq 4) that are conveniently observed through

$$(\mathrm{OEP})\mathrm{Rh\text{-}H} + \mathrm{CNR} \rightleftharpoons (\mathrm{OEP})\mathrm{Rh(H)(RNC)} \tag{4}$$

changes in the hydride ^{1}H NMR resonance. The hydride NMR resonance for (OEP)Rh-H ($\delta_{\mathrm{Rh\text{-}H}} = -41.5$ ppm; $J^{103}{}_{\mathrm{Rh\text{-}H}} = 44$ Hz) shifts by $\sim$11–12 ppm to lower field, and the ^{103}Rh-H coupling decreases by $\sim$24–27 Hz upon adduct formation with the isocyanides studied. The largest change in Rh-H chemical shift and ^{103}Rh-H coupling occurs for the methyl isocyanide complex ($\delta_{\mathrm{Rh\text{-}}H} = -27.9$ ppm; $J^{103}{}_{\mathrm{Rh\text{-}H}} = 16.8$ Hz) followed by the complexes of *n*-butyl isocyanide ($\delta_{\mathrm{Rh\text{-}}H} = -29.3$ ppm; $J^{103}{}_{\mathrm{Rh\text{-}H}} = 18.5$ Hz) and 2,6-dimethylphenyl isocyanide ($\delta_{\mathrm{Rh\text{-}}H} = -29.8$ ppm; $J^{103}{}_{\mathrm{Rh\text{-}H}} = 19.0$ Hz).

Subsequent to isocyanide coordination a slower reaction occurs between the (OEP)Rh—H species and excess isocyanide to produce formimidoyl complexes, (OEP)-Rh—CH=NR (eq 5). Production of formimidoyl com-

$$(\mathrm{OEP})\mathrm{Rh(H)(CNR)} + \mathrm{RNC} \rightleftharpoons (\mathrm{OEP})\mathrm{Rh(CH{=}NR)(RNC)} \tag{5}$$

plexes from alkyl isocyanides is accompanied by appearance of alkyl and cyanide complexes (eq 2), but the CN—R cleavage reaction is quenched when 2,6-dimethylphenyl isocyanide is used for reaction 5. Formation of the formimidoyl species in solution is most easily followed by appearance of the relatively high field resonances of the *N*-alkyl or *N*-aryl groups (Figure 4). The most diagnostic ^{1}H NMR peak for (OEP)Rh—CH=NR complexes is the formimidoyl C—H resonance which occurs as a doublet at $\delta = 0.52$ ppm ($J^{103}{}_{\mathrm{Rh\text{-}CH}} = 2.7$ Hz) in the five-coordinate 2,6-dimethylphenyl derivative (Figure 4) and shifts to $\delta = 1.33$ ppm ($J^{103}{}_{\mathrm{Rh\text{-}CH}} = 3.0$ Hz) in the presence of a large excess of the free isocyanide. The formimidoyl C—H peak for the *n*-butyl derivative in the presence of excess isocyanide occurs at $\delta = 1.28$ ppm ($J^{103}{}_{\mathrm{Rh\text{-}CH}} = 2.9$ Hz).

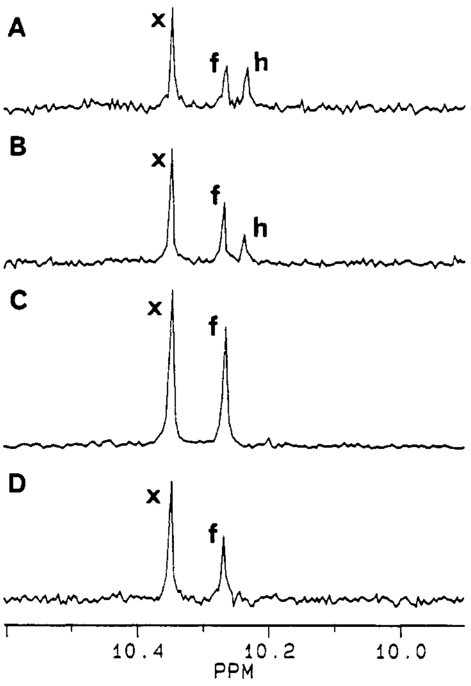


Figure 5. ^{1}H NMR (200-MHz) spectra for the porphyrin methine resonances for the reaction of $[(\mathrm{OEP})\mathrm{Rh}]_2$ with $C_6H_3(CH_3)_2NC$ and water (at 298 K in C_6D_6): (A) after 1 h; (B) after 1 day; (C) after 3 days; (D) after 15 days. ((x) (OEP)RhC(O)NHR; (f) (OEP)Rh—CH=NR; (h) (OEP)-Rh—H).)

The formimidoyl complexes were also identified by the parent ion in the FAB mass spectrum.

Reaction of Isocyanides and H_2O with $[(\mathrm{OEP})\mathrm{Rh}]_2$. Addition of water ($\sim 10^{-2}$ M) to a benzene solution of $[(\mathrm{OEP})\mathrm{Rh}]_2$ ($\sim 10^{-3}$ M) and 2,6-dimethylphenyl isocyanide ($\sim 10^{-2}$ M) results in formation of a carbamoyl complex together with (OEP)Rh—H which subsequently reacts with excess isocyanide to produce a formimidoyl complex (eqs 6 and 7) (Figure 5). Formation of the formimidoyl

$$[(\mathrm{OEP})\mathrm{Rh}]_2 + \mathrm{C_6H_3(CH_3)_2NC} + \mathrm{H_2O} \rightarrow (\mathrm{OEP})\mathrm{Rh{-}C(O)NH(C_6H_3(CH_3)_2)} + (\mathrm{OEP})\mathrm{Rh{-}H} \tag{6}$$

$$(\mathrm{OEP})\mathrm{Rh{-}H} + \mathrm{C_6H_3(CH_3)_2NC} \rightleftharpoons (\mathrm{OEP})\mathrm{Rh{-}CH{=}N(C_6H_3(CH_3)_2)} \tag{7}$$

from (OEP)Rh—H is relatively fast in the presence of $[(\mathrm{OEP})\mathrm{Rh}]_2$ but reaction 7 is very slow after the dimer is consumed in reaction 6. The carbamoyl complex always appears in higher concentration than the formimidoyl due to the loss of some (OEP)Rh—H to regenerate the dimer (eq 8). In a very slow reaction the formimidoyl complex

$$2(\mathrm{OEP})\mathrm{Rh{-}H} \rightleftharpoons [(\mathrm{OEP})\mathrm{Rh}]_2 + \mathrm{H_2} \tag{8}$$

reacts away to give the carbamoyl as the final thermodynamic product over a period of several months. The reactions of alkyl isocyanides (CH_3NC, *n*-BuNC, $\sim 10^{-2}$ M) with $[(\mathrm{OEP})\mathrm{Rh}]_2$ ($\sim 10^{-3}$ M) and water ($\sim 10^{-2}$ M) result in the formation of products derived from both reaction 6 and the CN—R bond cleavage reaction (eq 2). (OEP)Rh—CH_3 and (OEP)Rh(CN)(CH_3NC) are the predominant products of the reaction of $[(\mathrm{OEP})\mathrm{Rh}]_2$ and CH_3NC even in the presence of a large excess of H_2O. The reaction of $[(\mathrm{OEP})\mathrm{Rh}]_2$ with *n*-BuNC and H_2O gives

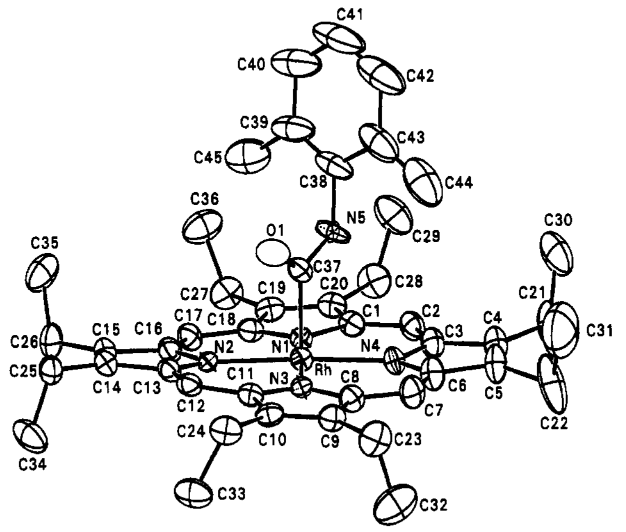


Figure 6. ORTEP view of (OEP)RhC(O)NH($C_6H_3(CH_3)_2$). Thermal ellipsoids are shown at the 30% probability level.

Table I. Crystal Data for (OEP)RhC(O)NH($C_6H_3(CH_3)_2$)

formula	$RhC_{45}H_{54}N_5O$
fw	783.87
cryst class	triclinic
space group	$P\bar{1}$ (No. 2)
Z	2
cell constants	
a, Å	12.256(3)
b, Å	13.234(2)
c, Å	15.075(3)
α, deg	61.79(2)
β, deg	75.89(2)
γ, deg	73.39(1)
V, Å^3	2047.7(7)
abs coeff, cm^{-1}	4.47
D_{calc}, g/cm^3	1.271
data collcn temp, °C	24
cryst dimens, mm	0.20 × 0.22 × 0.36
F(000)	824
Mo Kα radiation, λ, Å	0.710 73
θ range, deg	2.0–27.5
scan mode	ω–2θ
h,k,l collected	+15,±170±19
no. of reflns measd	9788
no. of unique reflns	9354
no. of reflns used in refinement	5587 ($F^2 > 3.0\sigma$)
no. of params	469
data/param ratio	11.9
R	0.051
R_w	0.058
GOF	1.446

(OEP)Rh—(n-Bu), (OEP)Rh(CN)(n-BuNC) and the carbamoyl complex as principal products.

The metallocarbamoyl complexes were independently prepared by the reaction of $[(OEP)Rh]_2$ with CO and the corresponding amines (eq 9). The metallocarbamoyl

$$[(OEP)Rh]_2 + 2CO + 2RNH_2 \rightarrow 2(OEP)Rh\text{–}C(O)NHR + H_2 \quad (9)$$

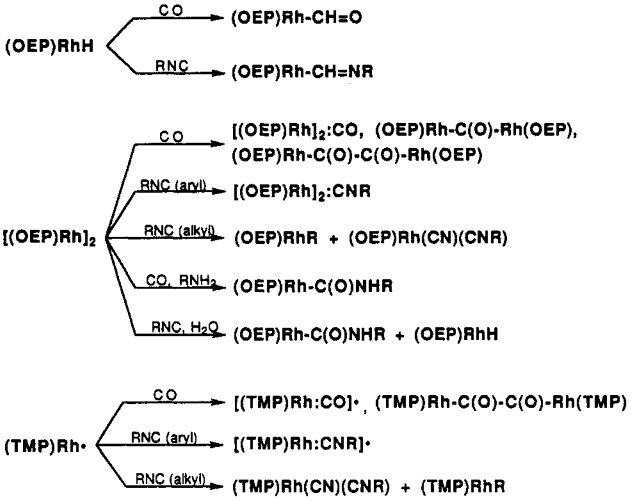
complex derived from 2,6-dimethylphenyl isocyanide was crystallized from benzene and characterized by single crystal X-ray structure determination (Figure 6). Table I summarizes the crystal data, and selected bond distances and angles for non-hydrogen atoms are given in Table II. The Rh atom deviates by 0.072 Å from the mean plane of the 4 pyrrole nitrogens and by 0.032 Å from the mean plane of the 24-atom core of the porphyrin ring.

Table II. Selected Bond Distances (Å) and Angles (deg) for (OEP)RhC(O)NH($C_6H_3(CH_3)_2$)[a]

Bond Distances			
Rh–N1	2.025(3)	Rh–C37	1.988(5)
Rh–N2	2.021(4)	C37–O1	1.197(6)
Rh–N3	2.026(3)	C37–N5	1.341(5)
Rh–N4	2.019(4)	C38–N5	1.444(7)
Bond Angles			
N1–Rh–N2	90.1(1)	N3–Rh–N4	89.8(1)
N1–Rh–N3	175.0(1)	N3–Rh–C37	91.2(2)
N1–Rh–N4	89.9(1)	N4–Rh–C37	92.0(2)
N1–Rh–C37	93.9(2)	Rh–C37–O1	122.1(3)
N2–Rh–N3	89.9(1)	Rh–C37–N5	114.6(4)
N2–Rh–N4	176.9(1)	N5–C37–O1	123.2(4)
N2–Rh–C37	91.1(2)	C37–N5–C38	123.0(5)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

Scheme I



Discussion

Reactivity studies of alkyl and aryl isocyanides with rhodium porphyrin species were undertaken for comparison with the unusual set of CO reactions that have been observed previously. A summary of these reactions is illustrated in Scheme I.

Carbon monoxide reacts with (OEP)Rh–H to produce a formyl complex[3] and with $[(OEP)Rh]_2$ to give an equilibrium distribution between a 1:1 complex (Rh–Rh:CO), a dimetal ketone (Rh–C(O)–Rh), and a dimetal diketone (Rh–C(O)C(O)–Rh)[1,6] (eqs 10–13). Each of these

$$(OEP)Rh\text{–}H + CO \rightleftharpoons (OEP)Rh\text{–}CHO \quad (10)$$

$$[(OEP)Rh]_2 + CO \rightleftharpoons [(OEP)Rh]_2CO \quad (11)$$

$$[(OEP)Rh]_2 + CO \rightleftharpoons (OEP)Rh\text{–}C(O)\text{–}Rh(OEP) \quad (12)$$

$$[(OEP)Rh]_2 + 2CO \rightleftharpoons (OEP)Rh\text{–}C(O)C(O)\text{–}Rh(OEP) \quad (13)$$

reactions is thought to occur through the intermediacy of a paramagnetic CO complex, $[(OEP)RhCO]^\bullet$, that reacts like an acyl radical.[1,11] Direct observation of the EPR spectrum of monocarbonyl species of this type, [(por)-

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[11] Paonessa, R. S.; Thomas, N. C.; Halpern, J. *J. Am. Chem. Soc.* **1985**, *107*, 4333.

RhCO]$^\bullet$, has been accomplished by using more sterically demanding porphyrins such as the tetramesityl derivative, (TMP)Rh$^\bullet$, which occurs as a stable metallo radical.[1,8] Analysis of the EPR parameters for [(TMP)-Rh^{13}CO]$^\bullet$ and related species indicates the presence of a nonlinear Rh–CO unit with substantial carbon spin density, and reactivity of these 17-electron monocarbonyls is dominated by one-electron reactions at the carbonyl carbon in a manner analogous to an acyl radical.[1]

Alkyl and aryl isocyanides react with (OEP)Rh—H to form 1:1 complexes (OEP)Rh(H)(RNC), that subsequently convert to formimidoyl species, (OEP)Rh—CH=NR (eq 5). Observation of adducts of (OEP)Rh—H with isocyanides (K_4(298 K) > 10^4) where the corresponding CO complex was not detected even at low temperatures in toluene solution (T = 200 K) illustrates the superior σ donor properties of isocyanides compared with CO. Production of formimidoyl complexes is directly analogous to the CO reaction that yields formyl complexes (eq 10). Addition of metal hydrides to isocyanides is thermodynamically more favorable than the corresponding reaction of CO[12] and thus the observation of formimidoyl complexes was anticipated on the basis of the prior observation of reaction 10. (OEP)Rh—CH=N($C_6H_3(CH_3)_2$) shows a $\upsilon_{C=N}$ band (KBr) at 1699 cm^{-1} that is substantially higher than the values reported for other metalloformimidoyls (1560–1630 cm^{-1}),[13,14] which probably results from relatively strong σ bonding and ineffective dπ–pπ back-bonding by the Rh(III) porphyrin group.

[(OEP)Rh]$_2$ exclusively forms 1:1 complexes with isocyanides and CO, where the equilibrium constants for isocyanide coordination (K_1(298 K) > 10^5) are much larger than the value for CO (K_{11}(298 K) = 48 ± 4).[6] EPR studies for (TMP)Rh$^\bullet$ with isocyanides and CO in toluene glass media also demonstrate the exclusive presence of 1:1 adducts. Similarity of the EPR parameters for [(TMP)-RhCNR]$^\bullet$ ($g_1 \sim g_2 \sim 2.16$; $g_3 = 1.995$; $A(^{103}\mathrm{Rh}) = 60$ MHz) and [(TMP)RhCO]$^\bullet$ ($g_1 \sim g_2 \sim 2.16$; $g_3 = 1.995$; $A(^{103}\mathrm{Rh}) = 67$ MHz) in toluene glass (90 K) suggest that these species have related electronic structures.

Alkyl isocyanides react further with (por)Rh^{II} compounds by CN–alkyl bond cleavage to form alkyl and cyanide complexes. Cleavage of the N–C single bond in isocyanides was accomplished previously by thermal decomposition of cationic transition-metal isocyanide complexes,[15-18] by thermolysis of (DMPE)$_2$Ru(naphthyl)H in the presence of *t*-BuNC,[19] and by the reaction of ($C_5Me_5)_2$Sm(THF)$_2$ with cyclohexyl and *tert*-butyl isocyanides.[20] The (por)Rh^{II} mediated R–NC cleavage reaction is unusual in that it results in the simultaneous incorporation of both the alkyl and CN units into a metal complex, as shown by formation of equal amounts of (por)Rh–CN and (por)Rh–R complexes.

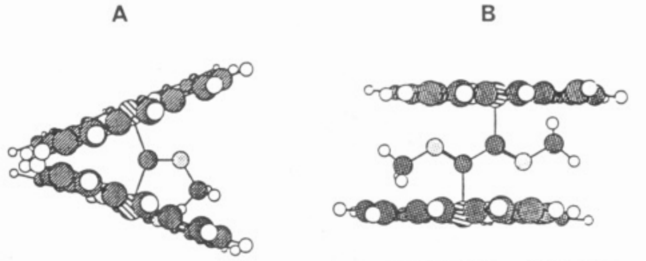

Figure 7. Structure simulations of (OEP)Rh–(CNCH$_3$)–Rh(OEP) (A) and (OEP)Rh–C(NCH$_3$)–C(NCH$_3$)–Rh(OEP) (B). (ethyl groups on the porphyrin rings are omitted for clarity.)

During this investigation no evidence was obtained for bridging imine (Rh–C(NR)–Rh) or diimine (Rh–C(NR)-C(NR)–Rh) species in contrast with reactions of CO that form dimetal ketone (Rh–C(O)–Rh) and dimetal diketone (Rh–C(O)C(O)–Rh) complexes.[6,7] Reduction and coupling are thermodynamically easier for isocyanides than they are for CO.[21] Absence of species containing bridging and coupled alkyl isocyanide units is most probably a consequence of the increased steric requirements of the isocyanide ligands compared to CO. Formation of dimetal imines, (OEP)Rh–C(NR)–Rh(OEP), is probably precluded by unfavorable interporphyrin interactions that are known to occur in bent one-atom bridged complexes such as the dimetal ketone,[7] (OEP)Rh–C(O)–Rh(OEP), as well as by additional interactions between the N–R group and the porphyrin ligands. Coupling of isocyanides in forming dimetal diimines, (OEP)Rh–C(NR)C(NR)–Rh(OEP), would relieve the interporphyrin repulsions, but unfavorable interactions occur between the *N*-alkyl and *N*-aryl groups and the two porphyrins which would encapsulate the organic fragment. Among the isocyanides studied only the coupling product from CH$_3$NC is sterically plausible, and in this case the relatively fast CH$_3$–NC cleavage reaction may preclude observation of this species. Structure simulations using Chem 3D illustrate the steric effects associated with the bridging and coupled isocyanide species (Figure 7).

Mechanistic Considerations. Alkyl and aryl isocyanide complexes with rhodium(II) porphyrin metallo radicals, [(por)RhCNR]$^\bullet$, may be important intermediates in isocyanide reactions in a manner analogous to the role of [(por)RhCO]$^\bullet$ species in CO reactions.[1,11] Reaction of [(por)RhCNR]$^\bullet$ with (por)Rh–H could be a pathway to produce formimidoyl complexes in analogy with the known role of [(por)RhCO]$^\bullet$ in producing formyl complexes.[11] The alkyl isocyanide N–alkyl bond cleavage reaction can be envisioned as occurring by either ionic or radical pathways.[15-20] Ligand induced disproportionation to form [(por)Rh(CNR)$_2$]$^+$ and [(por)Rh]$^-$ followed by nucleophilic attack of the anionic rhodium(I) fragment at the α-carbon of the alkyl group of the coordinated isocyanide is a plausible ionic mechanism. An alternate radical pathway could involve attack of a second metallo radical, (por)Rh$^\bullet$, at the isocyanide alkyl carbon of [(por)RhCN-R]$^\bullet$. Either reaction pathway would result in the concerted formation of (por)Rh(CN)(CNR) and (por)Rh–R through a trimolecular transition state similar to that suggested for the reactions of (por)Rh^{II} complexes with H$_2$ and hydrocarbons.[22,23] Absence of R–NC bond cleavage in the reaction of 2,6-dimethylphenyl isocyanide with (por)Rh^{II} complexes

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is a consequence of the steric demands associated with accommodating two (por)Rh units in a transition state where the porphyrin planes cannot be nearly parallel. A related argument has been invoked to explain why (por)Rh^{II} complexes activate methane but not aromatic C–H bonds.[23]

Reactions of isocyanides and water with $[(OEP)Rh]_2$ that produce carbamoyl complexes and (OEP)Rh—H (eq 6) probably involve addition of water to coordinated isocyanide to form an intermediate cationic hydroxycarbene which is subsequently deprotonated by $(OEP)Rh^-$ (eqs 14 and 15). Cationic hydroxycarbene complexes have

$$[(OEP)Rh]_2 + CNR + H_2O \rightarrow [(OEP)Rh{=}C(OH)NHR]^+[(OEP)Rh]^- \quad (14)$$

$$[(OEP)Rh{=}C(OH)NHR]^+ + [(OEP)Rh]^- \rightarrow (OEP)Rh{-}C(O)NHR + (OEP)Rh{-}H \quad (15)$$

previously been proposed as intermediates in the reactions of cationic isocyanide complexes, $[(OEP)Rh(CNR)_2]^+$, with water.[10] Reaction 14 could proceed through either the observed 1:1 complex $[(OEP)Rh]_2CNR$ or $[(OEP)Rh(CNR)_2]^+$ which may be formed by a donor induced disproportionation of $[(OEP)Rh]_2$. Pyridine is known to produce disproportionation of $[(OEP)Rh]_2$ to form $[(OEP)Rh(py)_2]^+$ and $[(OEP)Rh]^-$, but 2,6-dimethylphenyl isocyanide to $[(OEP)Rh]_2$ mole ratios of greater than 10^3 failed to produce ^1H NMR observable quantities of products associated with disproportionation. Formation of carbamoyl complexes through reaction of CO and RNH_2 with $[(OEP)Rh]_2$ could also occur through a hydroxycarbene intermediate, $[(OEP)Rh{=}C(OH)NHR]^+$.

More detailed kinetic–mechanistic studies are in progress which are directed toward distinguishing between radical and ionic reaction pathways of $[(OEP)Rh]_2$ that respectively involve homolysis or heterolysis of the Rh–Rh bond.

Experimental Section

General Methods. All manipulations were performed by vacuum line techniques or in an inert atmosphere box. NMR data were recorded on an IBM-Bruker WP 200SY instrument. Mass spectrometry results were obtained on a VG ZAB-E mass spectrometer using the fast-atom bombardment (FAB) method. EPR spectra were obtained by use of an EPR 100D X-band spectrometer. IR spectra were taken on a Perkin-Elmer 1760-X infrared Fourier transform spectrometer. Samples were prepared as either KBr pellets or Nujol mulls. Microanalytical data could not be obtained due to the small quantities of materials available. Structure simulations were performed with the Chem 3D Plus 3.0 molecular modeling program licensed from Cambridge Scientific Computing Inc.

Solvents and Reagents. Benzene and toluene were degassed by freeze–pump–thaw cycles and then refluxed over sodium/benzophenone until the solvent turned purple. Methyl isocyanide was prepared by the method of Weber and Ugi.[24] Syntheses of (TMP)Rh–CH_3, $[(OEP)Rh]_2$, and (OEP)Rh–H have previously been reported.[1,2] All other reagents were purchased from Aldrich or Fluka. Methyl, *n*-butyl, and 2,6-dimethylphenyl isocyanide were stored over type 4-Å molecular sieves to remove water.

Reactions of $[(OEP)Rh]_2$ with Isocyanides. Weighed samples of $[(OEP)Rh]_2$ (~0.5 mg) were placed in vacuum adapted NMR tubes and evacuated prior to vacuum transfer of both C_6D_6 (~0.5 mL) as solvent and variable quantities of an isocyanide (0.2–2.0 mg). The NMR tubes were sealed, and ^1H NMR was used in following the evolution of reaction products (T = 295 K).

Methyl Isocyanide. The reaction of CH_3NC with $[(OEP)Rh]_2$ yields a solution containing equal quantities of $(OEP)Rh(CH_3)(CH_3NC)$ and $(OEP)Rh(CN)(CH_3NC)$ as the exclusive products within a period of ~1 h. Excess isocyanide coordinates to the sixth coordination site of the rhodium–alkyl complex, causing a downfield shift of the porphyrin methine hydrogen resonance and an upfield shift of the axial methyl hydrogen resonance. The coordinated ligand is in fast exchange with uncoordinated isocyanide in the case of $(OEP)Rh(CH_3)(CH_3NC)$ and in slow exchange in the case of $(OEP)Rh(CN)(CH_3NC)$. Coordination of the isocyanide significantly enhances the solubility of the (OEP)Rh–CN complex which is virtually insoluble in C_6D_6 in the absence of excess isocyanide.

$(OEP)Rh(CH_3)(CH_3NC)$. ^1H NMR (δ in C_6D_6): 10.28 (s, 4H, porphyrin –CH=), 3.98 (m, 16H, CH_2CH_3), 1.91 (t, 24H, CH_2CH_3), –6.63 (d, 3H, axial CH_3, $^2J_{Rh-H}$ = 2.1 Hz). FAB MS: *m/e* 650 (calculated for (OEP)Rh—CH_3: *m/e* 650).

$(OEP)Rh(CN)(CH_3NC)$. ^1H NMR (δ in C_6D_6): 10.41 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.90 (t, 24H, CH_2CH_3), –1.76 (d, 3H, CN— CH_3). FAB MS: *m/e* 702 (calculated: *m/e* 702). IR: $\nu(C{\equiv}N)$ = 2235 cm^{-1}, 2131 cm^{-1} in KBr.

***n*-Butyl Isocyanide.** The reaction of *n*-BuNC with $[(OEP)Rh]_2$ gives $(OEP)Rh(CH_2CH_2CH_2CH_3)$(*n*-BuNC) and (OEP)Rh(CN)(*n*-BuNC) in equal amounts as exclusive products within a period of several hours. Coordination of excess isocyanide to the rhodium–alkyl complex has similar effects on the solubility and ^1H NMR as described above for methyl isocyanide.

$(OEP)Rh(CH_2CH_2CH_2CH_3)$(*n*-BuNC). ^1H NMR (δ in C_6D_6): 10.29 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, porphyrin CH_2CH_3), 1.90 (t, 24H, porphyrin CH_2CH_3), –1.01 (t, 3H, $RhCH_2CH_2CH_2CH_3$), –1.78 (m, 2H, $RhCH_2CH_2CH_2CH_3$), -4.65 (m, 2H, $RhCH_2CH_2CH_2CH_3$), –5.91 (m, 2H, $RhCH_2CH_2CH_2CH_3$). FAB MS: *m/e* 692 (calculated for (OEP)Rh(*n*-Bu): *m/e* 692).

(OEP)Rh(CN)(*n*-BuNC). ^1H NMR (δ in C_6D_6): 10.36 (s, 4H, porphyrin –CH=), 3.98 (m, 16H, porphyrin CH_2CH_3), 1.91 (t, 24H, porphyrin CH_2CH_3), –0.44 (t, 3H, $CNCH_2CH_2CH_2CH_3$), –0.86 (t, 2H, $CNCH_2CH_2CH_2CH_3$), –1.37 (m, 2H, $CNCH_2CH_2CH_2CH_3$), –1.56 (m, 2H, $CNCH_2CH_2CH_2CH_3$). FAB MS: *m/e* 744 (calculated: *m/e* 744). IR: $\nu(C{\equiv}N)$ = 2200 cm^{-1}, 2133 cm^{-1} in KBr.

2,6-Dimethylphenyl Isocyanide. The only reaction observed for 2,6-dimethylphenyl isocyanide is immediate 1:1 adduct formation where a single isocyanide is coordinated to the metal–metal bonded dimer. If the system contains more than a stoichiometric amount of isocyanide, the coordinated ligand is in fast exchange with the excess isocyanide present, making the two sides of the Rh–Rh bonded dimer appear to be equivalent in the ^1H NMR spectrum.

$[(OEP)Rh]_2((C_6H_3(CH_3)_2)NC)$ in the Presence of Excess Isocyanide. ^1H NMR (δ in C_6D_6): 9.05 (s, 8H, porphyrin –CH=), 4.46 (m, 16H, $CH_AH_BCH_3$), 4.00 (m, 16H, $CH_AH_BCH_3$), 1.68 (t, 48H, CH_2CH_3).

If less than a stoichiometric amount of isocyanide is present, the coordinated isocyanide is in slow exchange and the adduct displays two sets of porphyrin resonances and peaks associated with a coordinated isocyanide in the ^1H NMR spectrum.

$[(OEP)Rh]_2((C_6H_3(CH_3)_2)NC)$ in the Presence of Excess $[(OEP)Rh]_2$. ^1H NMR (δ in C_6D_6): 9.29 (s, 4H, porphyrin –CH=), 8.81 (s, 4H, porphyrin –CH=), 5.25 (t, 1H, phenyl para), 4.81 (d, 2H, phenyl meta), 4.54 (m, 8H, CH_AH_B—CH_3), 4.38 (m, 8H, CH_AH_B—CH_3), 3.99 (m, 16H, CH_ACH_B—CH_3), 1.68 (t, 48H, CH_2—CH_3), –1.50 (s, 6H, phenyl CH_3). IR: $\nu(C{\equiv}N)$ = 2160 cm^{-1} in Nujol.

Reactions of $[(OEP)Rh]_2$ with Isocyanides and Water. Weighed samples of $[(OEP)Rh]_2$ (~0.5 mg) were placed in vacuum adapted NMR tubes and evacuated prior to vacuum transfer of C_6D_6 (~0.5 mL), variable quantities of an isocyanide

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(0.2–2.0 mg), and excess H_2O (0.1–1.0 mg). The NMR tubes were sealed and ^1H NMR was used to follow the reactions (T = 295 K).

2,6-Dimethylphenyl Isocyanide. Addition of excess water to a solution of $[(OEP)Rh]_2$ and 2,6-dimethylphenyl isocyanide results in formation of the carbamoyl and metallohydride complexes over a period of 1 day. In a subsequent reaction the metallohydride compound reacts with the excess isocyanide to produce a formimidoyl complex.

$(OEP)Rh(C(O)NH(C_6H_3(CH_3)_2))((C_6H_3(CH_3)_2)NC)$. ^1H NMR (δ in C_6D_6): 10.36 (s, 4H, porphyrin –CH=), 5.98 (t, 1H, phenyl para), 5.80 (d, 2H, phenyl meta), 4.00 (m, 16H, CH_2CH_3), 1.90 (t, 24H, CH_2CH_3), –0.14 (s, 6H, phenyl CH_3), –1.28 (br, 1H, C(O)—NH–). FAB MS: m/e 783 (calculated for $(OEP)Rh(C(O)NH(C_6H_3(CH_3)_2))$: m/e 783). IR: ν(C=O) = 1676 cm^{-1} in KBr. Removal of the excess isocyanide from the system results in significant upfield shifts of the porphyrin methine peaks (10.36 to 10.24) and of the C(O)NH (–1.28 to –1.55) resonances.

Methyl Isocyanide and n-Butyl Isocyanide. Formation of the carbamoyl and formimidoyl compounds is in competition with the CN–R bond cleavage reaction, and all four products were observed in the reaction mixtures.

Reactions of (OEP)Rh–H with Isocyanides. Weighed samples of (OEP)Rh–H (~0.5 mg) were placed in vacuum adapted NMR tubes and evacuated prior to vacuum transfer of C_6D_6 (~0.5 mL) as solvent and variable quantities of an isocyanide (0.2–2.0 mg). The NMR tubes were sealed, and ^1H NMR spectroscopy was used in following the evolution of reaction products (T = 295 K).

Methyl Isocyanide. Immediate reaction of (OEP)Rh–H with CH_3NC results in formation of the 1:1 complex $(OEP)Rh(H)(CH_3NC)$, as evidenced by changes in the ^1H NMR, including a large downfield shift of the hydride resonance and decrease in the Rh–H coupling constant. In slower subsequent reactions the formimidoyl, alkyl, and cyanide complexes form over a period of several hours (T = 295 K).

$(OEP)Rh(H)(CH_3NC)$. ^1H NMR (δ in C_6D_6): 10.25 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.90 (t, 24H, CH_2CH_3), –27.9 (d, 1H, Rh—H, $^1J_{Rh-H}$ = 16.8 Hz).

$(OEP)Rh(CH{=}NCH_3)(CH_3NC)$. ^1H NMR (δ in C_6D_6): 10.34 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.93 (t, 24H, CH_2CH_3), 0.14 (s, 3H, N—CH_3). The resonance for the Rh—CH hydrogen was obscured by other peaks. FAB MS: m/e 677 (calculated for $(OEP)Rh(CH{=}NCH_3)$: m/e 677).

n-Butyl Isocyanide. Fast adduct formation is followed by insertion of an isocyanide molecule into the Rh–H bond, yielding the metalloformimidoyl compound as the major product in a few hours. In a parallel reaction some Rh–CN and Rh–alkyl also form as a result of a slower alkyl C–N bond cleavage reaction.

(OEP)Rh(H)(n-BuNC). ^1H NMR (δ in C_6D_6): 10.22 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.91 (t, 24H, CH_2CH_3), –29.3 (d, 1H, Rh—H, $^1J_{Rh-H}$ = 18.5 Hz).

$(OEP)Rh(CH{=}NCH_2CH_2CH_2CH_3)$(n-BuNC). ^1H NMR (δ in C_6D_6): 10.29 (s, 4H, porphyrin –CH=), 4.00 (m, 16H, porphyrin CH_2CH_3), 1.95 (t, 24H, porphyrin CH_2CH_3), 1.28 (d, 1H, RhCH=N–, $^2J_{Rh-H}$ = 2.9 Hz), 0.24 (t, 3H, $CH{=}NCH_2CH_2CH_2CH_3$), –0.11 (t, 2H, $CH{=}NCH_2CH_2CH_2CH_3$), –0.57 (m, 2H, $CH{=}NCH_2CH_2CH_2CH_3$), –0.88 (m, 2H, $CH{=}NCH_2CH_2CH_2CH_3$). FAB MS: m/e 719 (calculated for (OEP)Rh(CH=N-n-Bu): m/e 719).

2,6-Dimethylphenyl Isocyanide. Fast adduct formation is followed by exclusive formation of the formimidoyl product within 1 day.

$(OEP)Rh(H)((C_6H_3(CH_3)_2)NC)$. ^1H NMR (δ in C_6D_6): 10.23 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.90 (t, 24H, CH_2CH_3), –29.8 (d, 1H, Rh—H, $^1J_{Rh-H}$ = 19.0 Hz).

$(OEP)Rh(CH{=}N(C_6H_3(CH_3)_2))((C_6H_3(CH_3)_2)NC)$. ^1H NMR (δ in C_6D_6): 10.30 (s, 4H, porphyrin –CH=), 6.05 (t, 1H, phenyl para), 5.87 (d, 2H, phenyl meta), 4.02 (m, 16H, CH_2CH_3), 1.91 (t, 24H, CH_2CH_3), 1.33 (d, 1H, Rh—CH, $^2J_{Rh-H}$ = 2.7 Hz), –0.41 (s, 6H, phenyl CH_3). FAB MS: m/e 767 (calculated for $(OEP)Rh(CH{=}N(C_6H_3(CH_3)_2))$: m/e 767). IR: ν(C=N) = 1699 cm^{-1} in KBr. Removal of the excess isocyanide from the system results in upfield shifts of the porphyrin methine (10.30 to 10.09) and Rh—CH=N– (1.33 to 0.52) resonances.

Addition of excess CF_3COOH (~0.5 mg) to the 2,6-dimethylphenyl formimidoyl complex led to an immediate color change from orange to reddish-brown, presumably yielding the protonated complex.

$[(OEP)Rh(:CH{-}NH(C_6H_3(CH_3)_2)]^+CF_3COO^-$. ^1H NMR (δ in C_6D_6): 10.47 (s, 4H, porphyrin –CH=), 5.80 (t, 1H, phenyl para), 5.39 (d, 2H, phenyl meta), 4.03 (m, 16H, CH_2CH_3), 1.87 (t, 24H, CH_2CH_3), –0.96 (s, 6H, phenyl CH_3). The resonances for Rh—CH—NH– hydrogens were not found.

Reactions of $[(OEP)Rh]_2$ with CO and Amines. Weighed samples of $[(OEP)Rh]_2$ (~0.5 mg) were placed in vacuum adapted NMR tubes and evacuated prior to vacuum transfer of C_6D_6 (~0.6 mL) as solvent and variable quantities of methyl- and n-butylamine and 2,6-dimethylaniline. The NMR tubes were pressurized with ~400 Torr of carbon monoxide and sealed. ^1H NMR spectroscopy was used in following the evolution of the reaction products (T = 295 K).

Methylamine and n-Butylamine. The reactions reached completion by the time the ^1H NMR spectra were taken. Carbamoyl complexes ((OEP)RhC(O)NHR) formed as exclusive products observed in the ^1H NMR spectrum.

$(OEP)Rh(C(O)NH(CH_3))$. ^1H NMR (δ in C_6D_6): 10.27 (s, 4H, porphyrin –CH=), 3.99 (m, 16H, CH_2CH_3), 1.92 (t, 24H, CH_2CH_3), –0.31 (d, 3H, N—CH_3, $^3J_{H-H}$ = 4.8 Hz), –2.49 (br m, 1H, N—H). FAB MS: m/e 693 (calculated: m/e 693). IR: ν(C=O) = 1676 cm^{-1} in KBr.

$(OEP)Rh(C(O)NHCH_2CH_2CH_2CH_3)$. ^1H NMR (δ in C_6D_6): 10.29 (s, 4H, porphyrin –CH=), 4.00 (m, 16H, porphyrin CH_2CH_3), 1.92 (t, 24H, porphyrin CH_2CH_3), 0.29 (m, 2H, $NHCH_2CH_2CH_2CH_3$), 0.01 (t, 3H, $NHCH_2CH_2CH_2CH_3$), –0.58 (m, 2H, $NHCH_2CH_2CH_2CH_3$), –0.80 (m, 2H, $NHCH_2CH_2CH_2CH_3$), –2.63 (m, 1H, N—H). FAB MS: m/e 735 (calculated: m/e 735). IR: ν(C=O) = 1624 cm^{-1} in KBr.

2,6-Dimethylaniline. The reaction reached completion within 1 day, yielding the carbamoyl complex as the exclusive product observed by ^1H NMR.

Preparation of (OEP)Rh–CN and (TMP)Rh–CN. (OEP)Rh–CN and (TMP)Rh–CN were prepared by the reaction of (por)Rh–I (~10 mg) and excess AgCN (~3 mg) in 20 mL of dried ethanol. The mixture was stirred overnight at room temperature under argon atmosphere which resulted in the formation of an orange-red precipitate that was subsequently filtered out and washed with water and ethanol. The rhodium cyanide products are not soluble in $CDCl_3$ or C_6D_6, but addition of excess isocyanide resulted in slow dissolution over a period of several hours.

(OEP)Rh–CN. IR: ν(C≡N) = 2203 cm^{-1} in KBr. Anal. Calcd for $C_{37}H_{44}N_5Rh$: C, 67.17; H, 6.66; N, 10.59. Found: C, 66.84; H, 6.82; N, 10.32.

(TMP)Rh–CN. IR: ν(C≡N) = 2147 cm^{-1} in KBr. Anal. Calcd for $C_{57}H_{52}N_5Rh$: C, 75.25; H, 5.72; N, 7.70. Found: C, 74.81; H, 5.02; N, 8.12.

$(OEP)Rh(CN)((C_6H_3(CH_3)_2)NC)$. ^1H NMR (δ in C_6D_6): 10.38 (s, 4H, porphyrin –CH=), 5.67 (t, 1H, phenyl para), 5.25 (d, 2H, phenyl meta), 3.99 (m, 16H, CH_2CH_3), 1.88 (t, 24H, CH_2CH_3), –0.55 (s, 6H, phenyl CH_3). IR: ν(C≡N) = 2195, 2135 cm^{-1} in KBr.

Reactions of (TMP)Rh$^•$ with Isocyanides. Weighed samples of $(TMP)Rh{-}CH_3$ (~0.5 mg) were placed in vacuum adapted NMR tubes and evacuated prior to vacuum transfer of benzene (~0.5 mL) as solvent. The solutions were photolyzed for 6 h in a Rayonnet photoreactor (λ ≥ 350 nm) which is known to result in the complete conversion of $(TMP)Rh{-}CH_3$ to (TMP)Rh$^•$.[1] The benzene solution of (TMP)Rh$^•$ was evacuated to dryness followed by sequential vacuum transfer of C_6D_6 (~0.5 mL) and variable quantities of an isocyanide (0.2–2.0 mg).

Methyl Isocyanide. Immediate color change occurs upon addition of the CH_3NC to a benzene solution of (TMP)Rh$^•$. The

Table III. Refined Positional Parameters for (OEP)RhC(O)NH($C_6H_3(CH_3)_2$) and Their Estimated Standard Deviations[a]

atom	x	y	z	B_{eq}, Å^2	atom	x	y	z	B_{eq}, Å^2
Rh	0.17946(3)	0.03968(3)	0.39479(2)	3.166(7)	C22	0.2492(6)	–0.036(1)	0.0408(5)	10.7(4)
N1	0.0205(3)	0.1396(3)	0.4002(2)	3.47(9)	C23	0.5671(5)	–0.2609(4)	0.2976(4)	6.0(2)
N2	0.1975(3)	0.0274(3)	0.5295(2)	3.41(9)	C24	0.6053(4)	–0.2594(4)	0.5017(4)	4.8(1)
N3	0.3319(3)	–0.0727(3)	0.3959(2)	3.61(9)	C25	0.3633(4)	–0.0518(4)	0.7400(3)	4.7(1)
N4	0.1578(3)	0.0441(3)	0.2644(2)	3.9(1)	C26	0.1061(5)	0.1022(4)	0.7511(3)	5.4(1)
C1	–0.0514(4)	0.1939(4)	0.3256(3)	3.8(1)	C27	–0.2201(4)	0.3175(4)	0.5056(4)	5.4(1)
C2	–0.0269(4)	0.1803(4)	0.2367(3)	4.3(1)	C28	–0.2423(4)	0.3481(5)	0.2860(4)	5.9(2)
C3	0.0683(4)	0.1119(4)	0.2073(3)	4.3(1)	C29	–0.2054(6)	0.4586(6)	0.2028(5)	8.9(3)
C4	0.0917(4)	0.0999(4)	0.1135(3)	5.3(1)	C30	0.0344(6)	0.2915(7)	–0.0350(5)	9.6(3)
C5	0.1917(5)	0.0245(5)	0.1149(3)	5.7(1)	C31	0.333(1)	0.0325(8)	–0.0228(6)	15.3(4)
C6	0.2337(4)	–0.0097(4)	0.2087(3)	4.9(1)	C32	0.5240(7)	–0.3663(5)	0.3224(6)	9.8(2)
C7	0.3377(4)	–0.0846(4)	0.2388(3)	4.9(1)	C33	0.5751(5)	–0.3641(5)	0.5982(5)	6.4(2)
C8	0.3831(4)	–0.1144(4)	0.3255(3)	4.1(1)	C34	0.3624(5)	–0.1749(5)	0.8188(4)	7.4(2)
C9	0.4919(4)	–0.1927(4)	0.3540(3)	4.2(1)	C35	0.1011(6)	0.2319(5)	0.7138(4)	7.6(2)
C10	0.5081(4)	–0.1928(3)	0.4396(3)	3.9(1)	C36	–0.1854(6)	0.4296(5)	0.4851(5)	7.8(2)
C11	0.4076(4)	–0.1162(3)	0.4653(3)	3.7(1)	C37	0.2563(4)	0.1761(4)	0.3200(3)	3.9(1)
C12	0.3915(4)	–0.0909(3)	0.5476(3)	3.7(1)	C38	0.2342(4)	0.3810(5)	0.1941(4)	6.5(2)
C13	0.2940(4)	–0.0251(3)	0.5781(3)	3.5(1)	C39	0.1971(5)	0.4646(5)	0.2304(5)	7.9(2)
C14	0.2760(4)	–0.0060(4)	0.6678(3)	4.0(1)	C40	0.2372(6)	0.5685(5)	0.1734(6)	10.5(3)
C15	0.1671(4)	0.0581(4)	0.6741(3)	4.1(1)	C41	0.3085(7)	0.5863(7)	0.0837(7)	13.1(3)
C16	0.1184(4)	0.0806(3)	0.5855(3)	3.7(1)	C42	0.3410(6)	0.5054(7)	0.0458(6)	11.7(3)
C17	0.0115(4)	0.1458(4)	0.5611(3)	3.9(1)	C43	0.3043(5)	0.3957(7)	0.1032(5)	9.0(2)
C18	–0.0340(4)	0.1761(3)	0.4746(3)	3.7(1)	C44	0.3401(6)	0.3080(8)	0.0648(5)	10.7(3)
C19	–0.1416(4)	0.2562(4)	0.4447(3)	4.1(1)	C45	0.1203(6)	0.4432(6)	0.3267(6)	9.4(3)
C20	–0.1515(4)	0.2677(4)	0.3530(3)	4.0(1)	N5	0.1966(3)	0.2708(4)	0.2512(3)	5.9(1)
C21	0.0156(5)	0.1690(5)	0.0298(4)	7.1(2)	O1	0.3498(3)	0.1721(3)	0.3340(3)	5.6(1)

[a] $B_{eq} = {}^4/_3[\beta_{11}a^2 + \beta_{22}b^2 + \beta_{33}c^2 + \beta_{12}ab\cos\gamma + \beta_{13}ac\cos\beta + \beta_{23}bc\cos\alpha]$.

only NMR observable products were identified as Rh–CH_3 and Rh–CN complexes which form in equal quantities.

(TMP)Rh(CH_3)(CH_3NC). ^1H NMR (δ in C_6D_6): 8.79 (s, 8H, pyrrole), 7.19 (s, 4H, mesityl meta H), 7.09 (s, 4H, mesityl meta H), 2.44 (s, 12H, mesityl para CH_3), 2.14 (s, 12H, mesityl ortho CH_3), 1.83 (s, 4H, mesityl ortho CH_3), –5.79 (d, 3H, Rh–CH_3, $^2J_{Rh-H}$ = 2.2 Hz). FAB MS: *m/e* 898 (calculated for (TMP)Rh–CH_3: *m/e* 898).

(TMP)Rh(CN)(CH_3NC). ^1H NMR (δ in C_6D_6): 8.90 (s, 8H, pyrrole), 7.19 (s, 4H, mesityl meta H), 7.04 (s, 4H, mesityl meta H), 2.43 (s, 12H, mesityl para CH_3), 2.07 (s, 12H, mesityl ortho CH_3), 1.86 (s, 12H, mesityl ortho CH_3), –0.47 (s, 3H, N-CH_3). FAB MS: *m/e* 950 (calculated: *m/e* 950).

***n*-Butyl Isocyanide.** The reaction reaches completion within 30 min and yields Rh–CN and Rh–*n*-butyl complexes as exclusive products. The (TMP)Rh–CN precipitates and redissolves slowly in several hours.

(TMP)Rh($CH_2CH_2CH_2CH_3$)(*n*-BuNC). ^1H NMR (δ in C_6D_6): 8.77 (s, 8H, pyrrole), 7.20 (s, 4H, mesityl meta H), 7.07 (s, 4H, mesityl meta H), 2.43 (s, 12H, mesityl para CH_3), 2.15 (s, 12H, mesityl ortho CH_3), 1.99 (s, 12H, mesityl ortho CH_3), –0.52 (t, 3H, $RhCH_2CH_2CH_2CH_3$), –0.90 (m, 2H, $RhCH_2CH_2CH_2CH_3$), –3.93 (m, 2H, Rh–$CH_2CH_2CH_2CH_3$), –5.16 (m, 2H, Rh-$CH_2CH_2CH_2CH_3$). FAB MS: *m/e* 940 (calculated for (TMP)Rh–*n*-Bu: *m/e* 940).

(TMP)Rh(CN)(n-BuNC). ^1H NMR (δ in C_6D_6): 8.91 (s, 8H, pyrrole), 7.21 (s, 4H, mesityl meta H), 7.04 (s, 4H, mesityl meta H), 2.43 (s, 12H, mesityl para CH_3), 2.13 (s, 12H, mesityl ortho CH_3), 1.81 (s, 12H, mesityl ortho CH_3), 0.14 (t, 2H, $CNCH_2CH_2CH_2CH_3$), –0.25 (t, 3H, $CNCH_2CH_2CH_2CH_3$), –0.92 (m, 2H, $CNCH_2CH_2CH_2CH_3$), –0.94 (m, 2H, $CNCH_2CH_2CH_2CH_3$). FAB MS: *m/e* 992 (calculated: *m/e* 992).

X-ray Structure Determination of (OEP)RhC(O)NH($C_6H_3(CH_3)_2$). Purple crystals of the carbamoyl were obtained by slow evaporation of a benzene solution in air. The compound crystallizes in the triclinic space group $P\bar{1}$ with a = 12.256(3) Å, b = 13.234(2) Å, c = 15.075(3) Å, α = 61.79(2)°, β = 75.89(2)°, γ = 73.39(1)°, V = 2047.7(7) Å^3, Z = 2, and d_{calc} = 1.271 g/cm^3. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on an Enraf-Nonius CAD4 diffractometer employing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) and using the ϖ–2θ scan technique. A total of 9788 reflections were measured over the following ranges: $4 \leq 2\theta \leq 55°$, $0 \leq h \leq 15$, $-17 \leq k \leq 17$, $-19 \leq l \leq 19$. Three standard reflections measured every 3500 s of X-ray exposure showed no intensity decay over the course of data collection.

The intensity data were corrected for Lorentz and polarization effects but not for absorption. Of the reflections measured, a total of 5587 unique reflections with $F^2 > 3\sigma(F^2)$ were used during subsequent structure refinement.

The structure was solved by standard heavy atom Patterson techniques followed by weighted Fourier syntheses. Refinement was by full-matrix least-squares techniques based on F to minimize the quantity $\Sigma w(|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F)$. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were included as constant contributions to the structure factors and were not refined. Refinement converged to R = 0.051 and R_w = 0.058. Positional parameters are listed in Table III.

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Supplementary Material Available: Tables giving atomic coordinates, refined thermal parameters, bond distances, bond angles, and least-squares planes (12 pages). Ordering information is given on any current masthead page.

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