Preparation of (1,4,7-triazacyclononane)Rh(hydrocarbyl)$_3$ Compounds and Their Derivatives. Strong Donor Labilization of RhCl Bonds toward Alkylation and Preparation of Unusually Stable Alkyl Hydride Complexes of Rhodium

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(tacn)Rh(R)$_3$ compounds (tacn = 1,4,7-triazacyclononane; R = Me, Et, Ph, vinyl) have been prepared in 65−86% yields by treatment of (tacn)RhCl$_3$·H$_2$O with more than a 7-fold molar quantity of RLi in THF, followed by protonation by methanol. The product before protonation is (Li$_3$tacn)RhR$_3$ (Li$_3$tacn = 1,4,7-trilithio-1,4,7-triazacyclononane) which can be isolated. The alkylation is complete in a few minutes to a couple of hours, depending on R, which compares with 3−4 days for CnRhCl$_3$ with MeLi (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane) and suggests that the presumably first-formed (Li$_3$tacn)RhCl$_3$ is highly activated toward Cl$^-$ dissociation by the strong donor effect of the three LiNR$_2$ groups in the rhodium coordination sphere. Protonation of (Li$_3$tacn)RhR$_3$ by methanol gives the neutral products (tacn)RhR$_3$. X-ray structure determinations of (tacn)RhEt$_3$ and (tacn)RhPh$_3$ have been carried out. Protonolysis of (tacn)RhR$_3$ (R = Me, Et, Ph) by 2 HSO$_3$CF$_3$ (HOTf) affords (tacn)-RhR(OTf)$_2$. Dissolution of the latter in D$_2$O gives [(tacn)RhR(D$_2$O)$_2$](OTf)$_2$, which on standing for up to 2 days undergoes H/D exchange of the two NH groups trans to the aqua ligands. Treatment of (tacn)RhR(OTf)$_2$ with 1 equiv of PMe$_3$ followed by NaBH$_4$ or KBH$_4$ yields a mixture of [(tacn)Rh(H)R(PMe$_3$)](OTf) and [(tacn)Rh(H)$_2$(PMe$_3$)](OTf) which is separated by benzene extraction. Counterion exchange has been carried out where R = Me and Et with Na{B[C$_6$H$_3$-3,5-(CF$_3$)$_2$]$_4$} (NaBAr$^F_4$) yielding [(tacn)Rh(H)R(PMe$_3$)](BAr$^F_4$). Heating of [CnRh-(H)Et(PMe$_3$)]X (X = OTf or BAr$^F_4$), [(tacn)Rh(H)Et(PMe$_3$)]X, and [(tacn)Rh(H)Me(PMe$_3$)]X in C$_6$D$_6$ leads to formation of [(Cn/tacn)Rh(D)(C$_6$D$_5$)(L)]X in high yield in all cases. The half-lives of these cleanly first-order reactions at 80 °C are 1 min, 1.2 h, and 7.3 h, respectively, illustrating alkyl hydride thermal stabilities unprecedented in rhodium chemistry.

Introduction

When the initial investigations into the organometallic chemistry of "Cn"Rh^{III} (Cn = 1,4,7-trimethyl-1,4,7-triazacyclononane)[1] were conducted, the assumption was made that tertiary amines were necessary to allow the incorporation of alkyl groups at rhodium via the usual highly basic reagents such as RLi, RMgX, and R$_2$-Mg. We have recently found that this assumption is unwarranted, as alkylations of (tacn)RhCl$_3$ (tacn = 1,4,7-triazacyclononane) proceed rapidly and in good yields with several organolithium reagents. In fact, the alkylations are faster and cleaner than the corresponding reactions of CnRhCl$_3$, leading us to suppose that the intermediate (1,4,7-trilithio-1,4,7-triamidocyclononane)-RhCl$_3$ is highly activated toward halide dissociation by the strongly basic triamido trianion ligand. This versatile preparation of rhodium trihydrocarbyl complexes provides a convenient route for the preparation of hydrocarbyl hydrides of rhodium, three of which, [(tacn)-Rh(H)R(PMe$_3$)]$^+$ (R = Me, Et, Ph), are prepared and characterized herein. These alkyl hydride complexes are even more stable than the previously reported [CnRh(H)Me(PMe$_3$)]$^+$.[1c]

Results

Preparation of (tacn)RhR$_3$. Wieghardt[2] reported the synthesis of (tacn)RhCl$_3$·H$_2$O by heating a methanol−DMSO solution of tacn and RhCl$_3$·*n*H$_2$O at 90 °C, and this procedure generally affords 70−80% yields of the air-stable, yellow compound. This is then treated with an excess of RLi or ArLi in THF, followed by addition of methanol to yield the trihydrocarbyl complexes **1a−d** (Scheme 1). These alkylations can be examined conveniently by NMR spectroscopy in THF-*d*$_8$. Reaction with MeLi is complete in 2 h at ambient temperature, and that with EtLi, in 5 min. On a synthetic scale, THF was added to a solid mixture of (tacn)RhCl$_3$·H$_2$O and a 7−8-fold molar quantity of RLi at −78 °C, to avoid excess exotherm, and the solution was allowed to warm to room temperature. These were run for somewhat

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(1) (a) Wang, L.; Flood, T. C. *J. Am. Chem. Soc.* **1992**, *114*, 3169. (b) Wang, L.; Lu, R. S.; Bau, R.; Flood, T. C. *J. Am. Chem. Soc.* **1993**, *115*, 6999. (c) Wang, C.; Ziller, J. W.; Flood, T. C. *J. Am. Chem. Soc.* **1995**, *117*, 1647. (d) Wang, L.; Wang, C.; Bau, R.; Flood, T. C. *Organometallics* **1996**, *15*, 491. (e) Wang, L.; Sowa, J. R.; Wang, C.; Lu, R. S.; Gassman, P. G.; Flood, T. C. *Organometallics* **1996**, *15*, 4240. (f) Zhen, H.; Wang, C.; Hu, Y.; Flood, T. C. Submitted for publication.

(2) Wieghardt, K.; Schmidt, W.; Nuber, B.; Prinkner, B.; Weiss, J. *Chem. Ber.* **1980**, *113*, 36.

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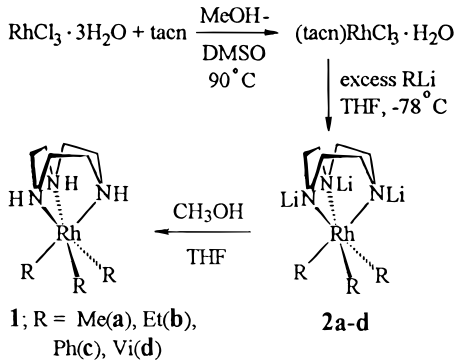
Scheme 1



longer times than the NMR experiments had indicated in order to ensure completion (see Experimental Section), but it is important not to let them go for much longer times (*e.g.*, 8 h), as this results in reduced yields. The initial product is the tris(lithium amide) **2** of which **2a** (R = Me) and **2b** (R = Et) have been isolated by evaporation of THF, extraction of excess RLi from the residue with ether or pentane, and then extraction of the product from the residue by (further) treatment with ether. Removal of the solvent under vacuum gave pale yellow (Li_3tacn)RhR_3, **2a**,**b** (Scheme 1). The ^{1}H and ^{13}C NMR spectra of **2b**, for example, are distinctly different from those of **1b** (see Experimental Section), and analysis of the lithium content of solid **2b** yielded a value of 5.69% (calcd, 6.18%). Protonation of lithium amides **2** is carried out in THF at room temperature with an excess of methanol, and solvent removal and product extraction with methylene chloride or benzene gives 65−86% yields of tris(hydrocarbyls) (tacn)RhR_3 (**1**; R = Me (**a**), Et (**b**), Ph (**c**), Vi (**d**); Scheme 1), which are all air and water stable and of considerable thermal stability. For example, **1b** is unaltered after 20 h in benzene-d_6 at 80 °C in a sealed tube.

All of the tris(hydrocarbyls) **1** show broad and/or complex ^{1}H NMR patterns for the tacn CH protons between δ 2.3 and 3.0 and broad NH singlets which are characteristically between δ 3.2 and 4.0 ppm in DMSO-d_6 or CD_3CN. In THF the spectrum of **1b** shows two broad singlets for the amine CH at δ 2.65 and 3.00, and the NH resonances are moved upfield underneath the peak at 3.00. In most solvents, protons on carbon bonded to rhodium (α-CH) are moved upfield from alkane values and, for example, are at δ −0.58 for RhMe and 0.32 for the RhEt methylenes in DMSO-d_6. All three vinyl CH protons are rhodium coupled in **1d**, but only the α-carbon is rhodium coupled in the ^{13}C spectrum. Benzene-d_6 has a unique effect on the proton spectrum of **1b**, showing the amine CH resonances as two sharp but complex second-order multiplets at δ 1.47 and 2.23 and the NH peaks upfield at δ 1.85. In addition, the methylene of the rhodium ethyl group is downfield at δ 1.15 ppm. The tris(*N*-methyl) complexes $CnRhR_3$ (R = Me, Et;[1d] R = Vi[1f]), analogues of **1**, show the same distinct ^{1}H NMR behavior in benzene solvent.

Structure Determinations of (tacn)$RhEt_3$ (1b) and (tacn)$RhPh_3$ (1c). Slow evaporation of a methylene chloride solution of **1b** resulted in formation of light yellow single crystals. Figure 1 shows a labeled molecular drawing of **1b**, and Table 1 lists selected bond parameters. The structure of the (tacn)Rh moiety shows features essentially the same as those of the tri-*N*-methylated CnRh molecules that bear three strong-field

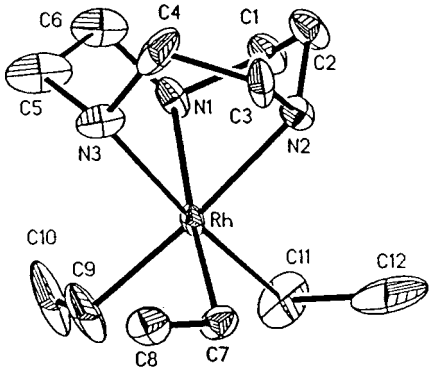


Figure 1. Molecular structure (50% probability) of the (tacn)$RhEt_3$ (**1b**) heavy atoms.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for (tacn)$RhEt_3$ (1b) and (tacn)$RhPh_3$ (1c)

	(tacn)$RhEt_3$ (**1b**)		
Rh−N(1)	2.209(3)	N(1)−Rh−N(2)	78.8(1)
Rh−N(2)	2.199(4)	N(2)−Rh−N(3)	79.3(1)
Rh−N(3)	2.192(4)	N(1)−Rh−N(3)	79.0(1)
Rh−C(7)	2.057(4)	C(7)−Rh−C(9)	86.8(2)
Rh−C(9)	2.047(5)	C(9)−Rh−C(11)	87.8(2)
Rh−C(11)	2.047(5)	C(7)−Rh−C(11)	87.1(2)
	(tacn)$RhPh_3$ (**1c**)		
Rh−N(1)	2.226(4)	N(1)−Rh−N(2)	78.4(1)
Rh−N(2)	2.200(4)	N(2)−Rh−N(3)	78.9(1)
Rh−N(3)	2.220(4)	N(1)−Rh−N(3)	78.5(1)
Rh−C(11)	2.025(4)	C(11)−Rh−C(21)	88.9(2)
Rh−C(21)	2.052(4)	C(21)−Rh−C(31)	92.4(2)
Rh−C(31)	2.022(4)	C(11)−Rh−C(31)	94.6(2)

unidentate ligands.[1c,d,f] An average N−Rh−N bond angle of 79° clearly indicates that the tacn ligand is moved away from the metal along the molecular 3-fold axis (not a crystallographic axis) to the same extent as the Cn ligand does in its $CnRhR_3$ complexes. The average Rh−N distance of 2.20 Å is slightly but probably significantly shorter than in the $CnRhR_3$ complexes which average 2.23 Å. Presumably this is the difference between secondary and tertiary Rh−N lengths. The Rh−C distances average 2.05 Å and the C−Rh−C angles average 87°, values indistinguishable from Cn-$RhMe_3$ and [*N*,*N*′,*N*″-tris(neohexyl)triazacyclononane]-$RhMe_3$.[1d] In the case of $CnRhMe_3$, the slightly acute C−Rh−C angle was attributed to steric congestion between the *Rh*-methyl and the *N*-methyl groups. Since there are no *N*-Me groups in **1b**, this explanation for $CnRhMe_3$ is unlikely, and an alternate explanation is not clear to us.

Solution of the X-ray diffraction data of **1c** generated the structure shown in Figure 2. Table 1 lists some of its bond parameters. As expected, structural features of the (tacn)Rh moiety are very similar to those of **1b**. *A priori*, because of the sp^2 carbon hybridization of the phenyl groups in **1c**, one might expect the Rh−C distances to be shorter in **1c** than in **1b**, and because of the differing trans influences of phenyl and ethyl, one might expect the Rh−N distances in **1c** to be slightly longer than those in **1b**. These expectations are consistent with the bond lengths in the two structures, except that the differences are of about the same size as 3σ and so must be regarded as only suggestive. Our attempts to prepare $CnRhPh_3$ have failed, so comparison to the Cn system is not possible. Two notable features of the **1c** structure are that there is a rather large variation in the C−Rh−C angles (94.6−88.9°), and the mutually trans Rh−C(21) and Rh−N(2) lengths are

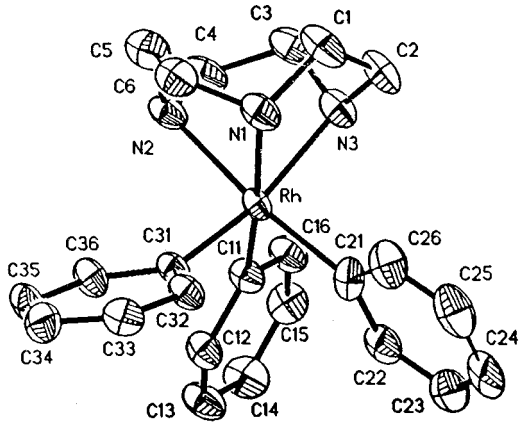
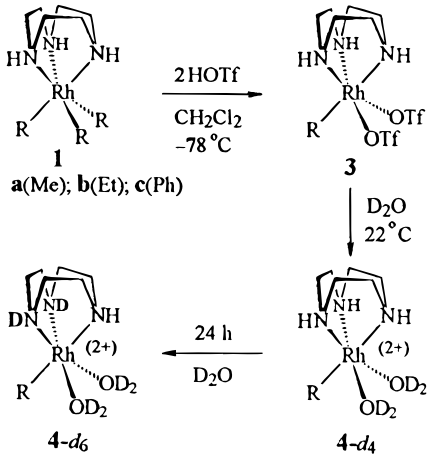


Figure 2. Molecular structure (50% probability) of the (tacn)$RhPh_3$ (**1c**) heavy atoms.

Scheme 2

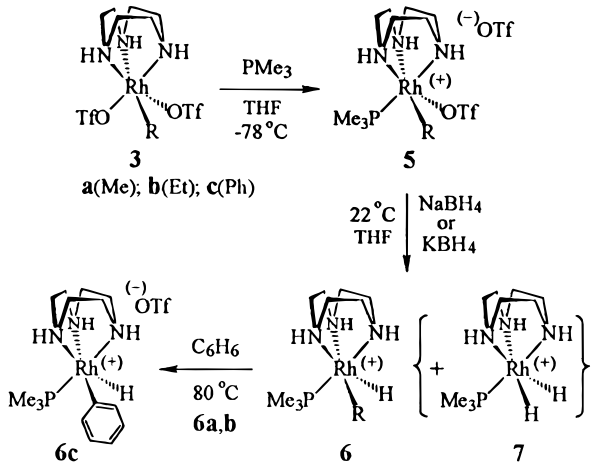


longer and shorter, respectively, than the other two pairs. These differences probably reflect the strong steric interaction of the three bulky phenyl groups.

Acid Cleavage of Rh−C Bonds. As is the case with $CnRhMe_3$,[1d] (tacn)RhR_3 complexes (**1a**−**c**; R = Me, Et, Ph) undergo Rh−C cleavage with 2 equiv of triflic acid ($HOS(O)_2CF_3$, HOTf) to afford (tacn)$RhR(OTf)_2$, **3a**−**c** (Scheme 2). Triethyl **1b** generates a complex mixture when treated with just 1 equiv of acid. $CnRhEt_3$ and 1 equiv of HOTf forms $CnRh(\pi\text{-}CH_2{=}CH_2)(OTf)$,[3] but apparently the tacn analogue is not stable. Trivinyl **1d** protonates at the vinyl methylene in the presence of 1 equiv of acid to form a cationic alkylidene complex which undergoes subsequent rearrangement to [(tacn)Rh-$(CH{=}CH_2)(\eta^3\text{-}CH_2CHCHMe)$](OTf). This latter chemistry using $CnRh(Vi)_3$ has been reported elsewhere.[1f] The (tacn)$RhR(OTf)_2$ compounds, **3a**−**c**, dissolve in D_2O to form materials assigned the structures [(tacn)RhR-$(D_2O)_2$](OTf)$_2$, **4a**−**c** (Scheme 2), which are all indefinitely stable in solution. The NH proton resonances of the tacn ligand of all three diaqua complexes show a clear pattern of two broad singlets at δ 5.65−5.86 and 5.90−6.35 ppm, with a 1:2 intensity ratio typical of materials with C_s symmetry. Gradually over a period of hours, the two-proton peak at lower field disappears, while the single-proton peak remains unchanged for much longer periods. Half-lives for exchange are slighly dependent on the hydrocarbyl ligand; $t_{1/2}$ for **4a** (Me) = 24 h and **4b** (Et) = 10 h, while the exchange of **4c** (Ph) is complete in less than 6 h. On the basis of the stoichiometry, we assign the exchange to the NH groups trans to the aqua ligands; apparently the NH trans to the hydrocarbyl does not H/D exchange with the solvent under conditions of simple dissolution at room temperature, but we have not checked for possible pH or temperature dependence of the exchange.

(3) Wang, C.; Flood, T. C. Unpublished results.

Scheme 3



Preparation of Alkyl Hydrides. One equivalent of trimethylphosphine in THF displaces triflate from **3a**−**c** and forms [(tacn)RhR(PMe_3)(OTf)](OTf), **5a**−**c** (Scheme 3); **5a**,**b** were isolated, while **5c** was prepared only *in situ*. An excess of PMe_3 must be avoided since disubstitution giving [(tacn)RhR$(PMe_3)_2$](OTf)$_2$ occurs very readily. This is in contrast to the analogue $CnRhMe(OTf)_2$, which forms only [$CnRhMe(PMe_3)$(OTf)]-(OTf) even with an excess of PMe_3.[1c] Reduction of **5** to hydrocarbyl hydride **6** was attempted with $LiBHEt_3$, $LiBH(sec Bu)_3$, and $LiAlH(O\text{-}t\text{-}Bu)_3$, but these gave complex mixtures that may come from reaction of the basic hydride with the NH bonds of the tacn ligand. Treatment of the salt **5** with $NaBH_4$ or KBH_4 in THF generates a mixture of [(tacn)Rh(H)R(PMe_3)](OTf), **6a**−**c**, and [(tacn)Rh$(H)_2(PMe_3)$](OTf), **7** (Scheme 3). The amount of **7** is highly variable: 10−50% with $NaBH_4$ and 60−95% with KBH_4. We have been unable to determine the source of this variability. Hydrocarbyl hydride **6** is sparingly soluble in benzene, while dihydride **7** is quite insoluble, so that separation of the two is possible although tedious. The benzene extraction also serves to separate **6** from insoluble excess $NaBH_4$ or KBH_4. Fortunately, dihydride **7** is inert to most of the chemistry that we wish to examine with the alkyl hydrides, and so moderate amounts can be tolerated in the sample. In some cases, it serves as a useful NMR internal standard. Small amounts of colored impurity are removed from **6a**,**b** and **7** by counterion exchange with Na{$B[C_6H_3\text{-}3,5\text{-}(CF_3)_2]_4$} ($NaBAr^F{}_4$) in chlorobenzene. The $^-BAr^F{}_4$ salts are designated **8a**,**b** and **9** to distinguish them from the triflate salts. In any event, preparation of pure alkyl hydrides can be achieved, but mixtures of **6** and **7** are suitable for most purposes.

Complexes **8a**,**b**, **6c**, and **9** have been fully characterized, including combustion analysis and/or high-resolution mass spectroscopy. In the ^1H NMR spectra of 6/8 the hydride resonance appears between δ −16.7 and −18.1 ppm (dd, $J_{RhH} \sim 28$ Hz, $J_{PH} \sim 36$ Hz), $P(CH_3)_3$ is a doublet ($J_{PH} \sim 9$−10 Hz) between δ 1.2 and 1.4 ppm, and NH appears as three broad singlets (the metal is chiral) between δ 4.7 and 5.8 ppm. $^{31}P\{^1H\}$ NMR resonances are doublets ($J_{RhP} \sim 136$−145 Hz) between

Table 2. Rate of Reaction of Rhodium Alkyl Hydride Cations at 80 °C in Benzene-d_6 (L = PMe_3)

compd	rate const (s^{-1})	half-life (min)
$[CnRh(H)Me(L)]^+$ [a]	$2.67(\pm0.20) \times 10^{-4}$	43
$[CnRh(H)Et(L)]^+$ [b]	$\approx 1 \times 10^{-2}$	≈ 1
$[(tacn)Rh(H)Me(L)]^+$	$2.65(\pm0.02) \times 10^{-5}$	436
$[(tacn)Rh(H)Et(L)]^+$	$1.60(\pm0.03) \times 10^{-4}$	72

[a] Reference 1c. [b] Rate constant at 56 °C is $1.97(\pm0.03) \times 10^{-4}$ s^{-1} ($t_{1/2}$ = 59 min).

δ 10.4 and 12.9 ppm, and off-resonance decoupling reveals a doublet of doublets for **6**/**8** and a doublet of triplets for **7**/**9**, confirming the dihydride structure of the last. As anticipated, the $^{13}C\{^1H\}$ NMR spectra of **6**/**8** show six tacn ligand resonances because of the metal chirality. The ethyl group α-carbon of **6b**/**8b** appears at δ −0.29 (dd, J_{RhC} = 26 Hz, J_{PC} = 11 Hz).

All three alkyl hydrides are stable enough for analysis by fast atom bombardment mass spectroscopy. Using FAB, signals at the masses of the intact cations are strong, and in the case of the phenyl hydride **6c**, it is the strongest signal. Also evident in each case is the mass corresponding to the ion $[(tacn)Rh(PMe_3)]^+$ from which the neutral hydrocarbon has been lost.

Thermolysis of Alkyl Hydrides. The relative stability (thermodynamic and kinetic) of metal alkyls is of current interest. We recently reported[1c] the preparation and some chemistry of $[CnRh(H)Me(PMe_3)]^+$. Its thermolysis in benzene results in loss of methane and the oxidative addition of the solvent to form $[CnRh(H)Ph(PMe_3)]^+$ essentially quantitatively. For purposes of comparison, we have also prepared the ethyl derivative $[CnRh(H)Et(PMe_3)]^+$, and it, **6a**, and **6b** all react with benzene at 80 °C to give high yields of the corresponding phenyl hydride complex. Half-lives for all of these reactions are given in Table 2. An estimate is given for $[CnRh(H)Et(PMe_3)]^+$ because its reaction was too fast at 80 °C to obtain a reliable value by NMR. The results shown in Table 2 clearly illustrate a substantial enhancement in stability for methyl over ethyl complexes and for tacn-ligated materials over the Cn analogues.

Discussion

For some time we had assumed that in order to prepare $(triamine)RhR_3$ via $(triamine)RhCl_3$ and reactive metallohydrocarbyls, the triamine ligand must contain only tertiary amines: certainly trianions such as $(Li_3tacn)RhCl_3$ or $(Li_3tacn)RhR_3$ (**2**) must be unstable. Nevertheless, we decided to attempt reaction of MeLi with $(tacn)RhCl_3$, which bears a trisecondary amine, and observed that the reaction is actually very clean and faster than reaction of MeLi with $CnRhCl_3$. Although solid **2** can be isolated, so far attempts to obtain crystallographic quality crystals have failed. We assume that three lithium ions are critical to the stability of $(Li_3tacn)RhX_3$ (X = halide or hydrocarbyl) and it is probable that they are tightly paired in THF solution. Given the fact that *species such as* **2** *are stable*, it is not surprising that the alkylation should proceed so well. The notion that basic lone pairs on ligands labilize a complex toward dissociation of another ligand dates back to 1937.[4a] The phenomenon of π-symmetry lone pairs labilizing mutually cis ligands has been studied in detail in classical coordination chemistry, particularly in the context of base-catalyzed hydrolysis of $[(NH_3)_5CoX]^{2+}$ and related systems.[4bc] Brown and co-workers[4d] delineated the importance of "cis effects" in carbonyl complexes such as $(CO)_5MnX$. For example, the rate ratio is 10^8 for CO substitution cis to the ligand X in $Cr(CO)_5X$ between X = Cl^- and X = PPh_3 and 10^{10} between X = Cl^- and X = CO.[4e] Since the early work of Brown, others have provided examples of the cis lone pair effect in other organometallic systems.[5] It is generally argued that strong π-electron pair donation of a ligand such as an amido group in a 5-coordinate, 16-electron fragment would cause the metal center to assume a trigonal bipyramidal geometry with the amido nitrogen and its lone pair lying in the equatorial plane. This would situate the plane of the amido group perpendicular to the equatorial plane of the TBP as in structure **I** (Figure 3).[6] It is difficult to see how the 5-coordinate, chloride-dissociated intermediate **II** could assume such an analogous geometry because the constraints of the tacn chelate would require two of the nitrogens to be equatorial and yet the N−Rh−N angle probably could not open very much from the *ca.* 80° characteristic of the octahedral tacn complexes. In addition, the nitrogen centers could not rotate and flatten in the same way as in **I**. Nevertheless, although spacial overlap with metal orbitals is expected to be poor, the electron pair is of π-symmetry with respect to the N−Rh axis and so some overlap with π-symmetry metal orbitals can still occur, and linear combinations of the three nitrogen lone pairs give considerable flexibility to the amido lone pairs for symmetry matching for π donation. Thus, the two unidentate ligands in the 5-coordinate intermediate could also reorganize to optimize stabilization of the coordinative unsaturation of the metal center. These last two effects are pictured in hypothetical structure **III**, where two nitrogens and a third ligand form a "Y"-shaped equatorial array about the metal with a π-symmetry linear combination of their lone pairs available for approximately equatorial-plane donation. Last, the field effects from

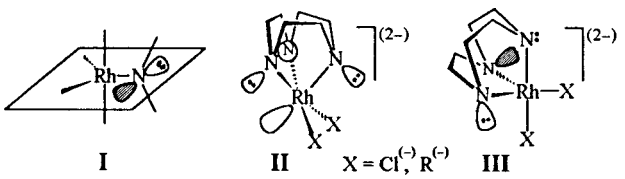


Figure 3. Schematic representation of the symmetry properties of amido ligands in potential overlap with the rhodium center. Lithium counterions have been omitted for clarity. See the text and note 6.

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(6) Although the lithium ions have been omitted from Figure 3 for clarity, they are almost certainly tightly associated in solution as well as in the solid. However, wherever the lithium ions are located, they will have no effect on the symmetry of overlap of the nitrogen lone pairs with the rhodium center. In addition, while the coulombic stabilization of the anion by the cations must be critically important, the bonding is probably essentially completely ionic, and so the lithium cations can relocate to accommodate the redistribution of negative charge within the rhodium complex. Thus, they probably have minimal effects on the extent of charge redistribution by orbital overlap of the nitrogens with rhodium.

three facial, anionic nitrogen ligands are difficult to estimate; they could be influential in ejecting an anionic ligand from the metal. In any event, it is clear that the amido groups are not without effect, since substitution is so much faster for (tacn)$RhCl_3$ than $CnRhCl_3$. These substitutions afford a general entry into the organo−Rh(tacn) system.

A pleasant surprise regarding the (tacn)Rh system in general is that while solubilities of analogous (tacn)Rh and CnRh molecules are frequently somewhat different and solubility for either type of molecule is often quite limited, nevertheless, the solubility of the (tacn)Rh species are not generally diminished in aromatic and polar organic solvents compared to the CnRh congeners. Another encouraging finding is that, contrary to our initial concern that (tacn)Rh alkyls might eliminate alkane by protonolysis from the rather acidic intramolecular N−H bonds, to date we have seen no indications of intramolecular RH elimination. Perhaps this is not surprising in view of the effective precedent[1b] of $[CnRhMe(H_2O)_2]^{2+}$ being stable indefinitely at ambient temperature in aqueous solution. Of course, we now know that $[(tacn)RhR(H_2O)_2]^{2+}$, **4a**−**c**, are all similarly stable in water, and the hydrocarbyl groups are certainly less likely to react with the intramolecular NH protons than with the much more acidic protons of coordinated water.

The most obvious mechanisms for H/D exchange of the N−H groups in $[(tacn)RhR(D_2O)_2]^{2+}$, **4a**−**c**, in D_2O (Scheme 2) are (a) ionization of the N−H bond of the intact complex and (b) dissociation of an amine center from the rhodium in the otherwise intact ion long enough to undergo normal proton exchange with the deuterated solvent. Useful information is available from a previously reported[1b] X-ray structure determination of the closely related $[CnRhMe(H_2O)_2]^{2+}$, wherein a large difference in trans influence of the strong-field methyl group and weak-field aqua ligands on the Rh−N bond distances is evident. Lengths for the Rh−N bonds trans to H_2O are 2.04(2) and 2.07(2) Å, while that trans to methyl is 2.21(1) Å—differences of *ca*. 7%! Assuming that the structure of $[(tacn)RhR(D_2O)_2]^{2+}$, **4**, would possess the same differences and taking the shorter bonds to be stronger and therefore slower to dissociate, the Rh−N dissociation explanation for H/D exchange in **4b** seems very unlikely. On the other hand, a substantially stronger Rh−N bond could reasonably be expected to render the N−H bond more acidic and therefore faster to exchange by an ionization mechanism.

The thermolysis of alkyl hydride complexes of the late transition metals is now a well-known method for the generation of reactive metal species capable of re-adding C−H bonds of alkanes,[7] arenes,[7b−e,g,k,8] and alkenes.[7b,d,9] In general, alkyl hydride complexes of rhodium have been much less stable to alkane loss than their iridium analogues. For example, loss of methane from Cp*Ir(H)Me(PMe_3) requires temperatures in excess of 150 °C,[7e] while Cp*Rh(H)Me(PMe_3) loses methane at −17 °C.[7b] Cp*Rh(H)Et(PMe_3) was prepared below −60 °C and loses ethane at −30 °C.[7f] On the other hand, the anionic ligand tris(2,3-dimethylpyrazolyl)borate (tpb*) seems to impart greater stability to rhodium alkyl hydrides: (tpb*)Rh(CO)(H)Me persists at room temperature for hours,[7g] and (tpb*)Rh(CN-*t*-Bu)(H)Me loses methane at 23 °C with $t_{1/2} = 5.6$ h.[7k] Thus, the half-life for methane loss of *ca*. 7 h at 80 °C exhibited by $[(tacn)Rh(H)Me(PMe_3)]^+$, **6a**, is a remarkable stability for a rhodium alkyl hydride. This particular stability for the $[(tacn)Rh(H)R(PMe_3)]^+$ series places them in a range where they are stable enough for convenient synthesis and characterization and yet reactive enough to study under conditions where the chemistry is more likely to remain relatively clean and free of decomposition to catalytic impurities. Thus, synthetic and mechanistic investigations of (tacn)Rh(H)R(X) with hydrocarbyl ligands R intended to address specific questions with assorted neutral and anionic ligands X are the objects of our continuing efforts.

Experimental Section

General Methods. All reactions involving organometallic compounds, unless otherwise mentioned, were carried out under an atmosphere of N_2 or Ar purified over reduced Cu catalyst (BASF R3-11) and Aquasorb. Flamed-out glassware and standard vacuum line, Schlenk, and N_2-atmosphere box techniques were employed. Benzene, ether, hexanes, pentanes, and THF were distilled from purple solutions of sodium/benzophenone, and CH_2Cl_2 were distilled twice from CaH_2. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. High-resolution FAB MS were recorded at the Mass Spectroscopy Facility of the University of California at Riverside. NMR chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane for ^1H and ^{13}C.

Materials. Concise preparations of tacn, Cn, and $CnRhCl_3$ have recently been published.[1d] $NaBAr^F{}_4$[10] and EtLi[11] were literature preparations. Et_2Mg was prepared from EtMgBr by the standard dioxane method,[12] and ViLi was prepared from $SnVi_4$.[13] PhLi, MeLi, EtMgBr, MeMgBr, $SnVi_4$, all other reagents, and all solvents were commercial materials.

(tacn)$RhCl_3$·H_2O.[2] A solution of tacn (2.20 g, 17.1 mmol) in 17 mL of methanol was added dropwise to a stirred solution of $RhCl_3$·$3H_2O$ (4.49 g, 17.1 mmol) in 80 mL of DMSO (dried over 3 Å molecular series) at RT (room temperature). The color of the solution changed to light red. After a few minutes, heating was commenced at 90 °C for 2 h, during which a copious yellow precipitate formed. The supernatant was decanted, and the precipitate was washed with DMSO (2 × 30 mL), water (3 × 30 mL), ethanol (3 × 30 mL), and ether (3 × 30 mL), and air-dried to yield 4.4 g of yellow solid (72%). The product was too insoluble to obtain spectra.

(tacn)$RhMe_3$ (1a). THF (60 mL) was slowly added to a stirred mixture of (tacn)$RhCl_3$·H_2O (0.40 g, 1.1 mmol) and solid

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halide-free CH_3Li (0.250 g 11.2 mmol) in a −78 °C bath. The mixture was allowed to warm to RT, and after 3 h of stirring a clear yellow solution was obtained. The solvent was evaporated under vacuum, and the residue was washed with ether (3 × 40 mL) to extract excess CH_3Li, each time decanting by cannula. The residue was dried under vacuum to give a white solid. The material assigned the structure (Li_3tacn)$RhMe_3$ (**2a**) exhibited the following spectra. ^{1}H NMR (DMSO-d_6, 360 MHz): δ −0.58 (d, J_{RhH} = 2.0 Hz, RhCH_3), 2.4−2.85 (m, NCH_2). ^{13}C NMR (DMSO-d_6, 90 MHz): δ −6.58 (dq, J_{RhC} = 34 Hz, J_{CH} = 119 Hz, RhCH_3), 47.12 (t, J_{CH} = 134 Hz, NCH_2). For protonation of the amido groups, the solid (Li_3tacn)$RhMe_3$ was dissolved in 70 mL of THF and 3.0 mL of MeOH (excess) was added with stirring. Stirring was continued for 20 min, and then the volatiles were removed under vacuum to give a cream-colored solid. The solid was extracted with CH_2Cl_2 (3 × 30 mL), and the extract was filtered and evaporated to yield a light yellow solid (0.20 g, 65%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ −0.58 (d, J_{RhH} = 2.6 Hz, RhCH_3), 2.46−2.78 (m, NCH_2), 3.67 (brs, NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 90 MHz): δ −6.57 (d, J_{RhC} = 34 Hz, RhCH_3), 47.22 (NCH_2). Anal. Calcd for $C_9H_{24}N_3Rh$: C, 38.99; H, 8.73; N, 15.16. Found: C, 38.52; H, 8.82; N, 14.45.

(tacn)RhEt$_3$ (1b). The procedure was the same as for (tacn)$RhMe_3$ using 0.38 g of (tacn)$RhCl_3$·H_2O (1.1 mmol), 0.38 g of EtLi (8.4 mmol), and 40 mL of THF. After 45 min at RT the THF was removed under vacuum and the residue was extracted with pentane (4 × 40 mL) to remove excess EtLi. Protonation was carried out in 40 mL THF with 2 mL of MeOH. This residue was extracted with benzene (3 × 40 mL), and a light-yellow solid (0.25 g 74%) was obtained. Slow evaporation of a CH_2Cl_2 solution of the product gave single crystals suitable for crystallography. ^{1}H NMR (DMSO-d_6, 360 MHz): δ 0.32 (dq, J_{RhH} = 2.8 Hz, J_{HH} = 8 Hz, RhCH_2), 0.78 (t, RhCH_2CH_3), 2.53−2.82 (m, NCH_2), 3.19 (brs, NH). ^{1}H NMR (C_6D_6, 360 MHz): δ 1.15 (dq, RhCH_2), 1.32 (t, RhCH_2CH_3), 1.42−1.56 (m, NCH_2), 1.85 (br s, NH), 2.20−2.27 (m, NCH_2). ^{1}H NMR (THF-d_8, 360 MHz): δ 0.48 (dq, RhCH_2), 0.84 (t, RhCH_2CH_3), 2.65 (brs, 6H, NCH_2), 3.00 (br s, 9H, NCH_2 and NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 63 MHz): δ 9.20 (d, J_{RhC} = 36 Hz, RhCH_2), 18.16 (RhCH_2CH_3), 47.09 (NCH_2). Anal. Calcd for $C_{12}H_{30}N_3Rh$: C, 45.14; H, 9.47; N, 13.16. Found: C, 45.13; H, 9.33; N, 12.83.

(Li_3tacn)RhEt$_3$ (2b). The initial product from reaction of (tacn)$RhCl_3$·H_2O and EtLi in the preparation of **1b** above was extracted with pentane to remove excess EtLi. The residue was then extracted with ether to separate **2b** from insoluble salts. The ether was removed and the product dried under vacuum. ^{1}H NMR (THF-d_8, 360 MHz): δ −0.15 (dq, J_{RhH} = 2.2 Hz, J_{HH} = 7 Hz, RhCH_2), 1.02 (t, RhCH_2CH_3), 2.58 (br s, NCH_2). ^{13}C{^{1}H} NMR (THF-d_8, 90 MHz): δ −1.50 (d, J_{RhC} = 29 Hz, RhCH_2), 14.48 (RhCH_2CH_3), 59.65 (NCH_2). Anal. Calcd for $C_{12}H_{27}N_3Li_3Rh$: Li, 6.18. Found: Li, 5.69.

(tacn)RhPh$_3$ (1c). The procedure was the same as for (tacn)$RhMe_3$ using 0.30 g of (tacn)$RhCl_3$·H_2O (0.84 mmol), 0.71 g of PhLi (8.4 mmol), and 50 mL of THF. After 45 min at RT the THF was removed under vacuum and the residue was extracted with pentane (4 × 40 mL) to remove excess PhLi, and protonation was carried out in 30 mL THF with 2.5 mL of MeOH. This residue was extracted with CH_2Cl_2 (2 × 50 mL), and a light yellow solid (0.31 g 80%) was obtained. Slow evaporation of a CH_2Cl_2 solution of the product gave light yellow crystals suitable for crystallography. ^{1}H NMR (DMSO-d_6, 250 MHz): δ 2.44−2.52 (m, 6H, NCH_2), 2.80−2.92 (m, 6H, NCH_2), 4.45 (br s, NH), 6.54−7.34 (m, RhC_6H_5). ^{13}C{^{1}H} NMR (DMSO-d_6, 90 MHz): δ 47.91 (NCH_2), 118.50 (Ph), 124.58 (2C, Ph), 139.99 (2C, Ph), 169.70 (d, J_{RhC} = 40 Hz, Ph). Anal. Calcd for $C_{24}H_{30}N_3Rh$: C, 62.20; H, 6.52; N, 9.07. Found: C, 62.88; H, 6.29; N, 8.59. FAB mass spectrum from CH_2Cl_2−nitrobenzyl alcohol−NaCl matrix volatilized [(tacn)$RhPh_3Na$]$^+$: Calcd for [$C_{24}H_{30}N_3Rh$]Na^+, *m/e* 486.1392; found, *m/e* 486.1373 (1.7%) (4 ppm). Also observed, *m/e* = 462 (3.5%) [M^+ − H], 386 (4%) [M^+ − C_6H_5], 309 (15%) [M^+ − $C_{12}H_{10}$].

(tacn)RhVi$_3$ (1d). THF (40 mL) was slowly added to a stirred mixture of (tacn)$RhCl_3$·H_2O (0.25 g, 0.70 mmol) and solid vinyllithium (0.23 g, 7.0 mmol) in a −78 °C bath. The mixture was allowed to warm to RT, and after 20 min a clear light brown solution had formed. After an additional 1 h of stirring, 1.5 mL of MeOH was added resulting in evolution of gas and formation of solids. The mixture was stirred for 30 min, the volatiles were removed under vacuum, and the residue was extracted with CH_2Cl_2 (2 × 40 mL). The extract was filtered, and the solvent was removed under vacuum to give a light yellow solid (0.19 g, 86%). ^{1}H NMR (DMSO-d_6, 250 MHz): δ 2.38−2.97 (m, NCH_2), 3.98 (br s, NH), 4.95 (ddd, $J_{H_aH_b}$ = 3.6 Hz, $J_{H_aH_c}$ = 18 Hz, J_{RhH_a} = 1.8 Hz, RhCH=CHH_a cis to Rh), 5.30 (ddd, $J_{H_bH_c}$ = 10 Hz, J_{RhH_b} = 3.5 Hz, RhCH=CHH_b trans to Rh), 7.60 (ddd, J_{RhH_c} = 1.6 Hz, RhCH_c=CH_2). ^{13}C{^{1}H} NMR (DMSO-d_6, 63 MHz): δ 47.06 (NCH_2), 113.64 (=CH_2), 172.20 (d, J_{RhC} = 39 Hz, RhCH=). Anal. Calcd for $C_{12}H_{24}N_3Rh$: C, 46.01; H, 7.72. Found: C, 45.42; H, 7.69. FAB mass spectrum: Calcd for [$C_{12}H_{24}N_3Rh$]-H^+, *m/e* 314.1104; found, *m/e* 314.1088 (92%) (5 ppm). Also observed, *m/e* = 288 (52%) [MH^+ − C_2H_2].

(tacn)RhMe(OTf)$_2$ (3a). A 3.30-mL portion of a 0.245 N solution of HOTf (0.81 mmol) in ether was slowly added to a stirred solution of 0.12 g (0.43 mmol) of (tacn)$RhMe_3$ in 90 mL of CH_2Cl_2 in a −78 °C bath. After 5 min at −78 °C, the solution was allowed to warm, and after 40 min at RT a voluminous light-orange precipitate had formed. The supernatant was decanted by cannula, and the precipitate was washed with CH_2Cl_2 (3 × 20 mL) and dried under vacuum to give a light orange solid (0.21 g, 91%). Anal. Calcd for $C_9H_{18}N_3F_6O_6S_2Rh$: C, 19.82; H, 3.33; N, 7.71. Found: C, 19.95; H, 3.18; N, 7.73. NMR spectra were recorded in D_2O solvent, hence they are of **[(tacn)RhMe(D_2O)$_2$](OTf)$_2$ (4a-d_4)**. ^{1}H NMR (D_2O, 360 MHz): δ 1.54 (d, J_{RhH} = 2.1 Hz, RhCH_3), 2.67−3.49 (m, NCH_2), 5.86 (br s, 1H, NH), 6.35 (br s, 2H, NH). ^{13}C{^{1}H} NMR (D_2O, 90 MHz): δ −3.64 (d, J_{RhC} = 24 Hz, RhCH_3), 46.23, 51.47, 53.31 (3s, NCH_2). The downfield NH proton peak at δ 6.35 disappeared with an approximate half-time of 24 h.

(tacn)RhEt(OTf)$_2$ (3b). The procedure was the same as for **3a**, using 5.0 mL of a 0.245 N solution of HOTf (1.2 mmol) in ether and 0.21 g (0.64 mmol) of (tacn)$RhEt_3$ in 70 mL of CH_2Cl_2. The precipitate was washed with CH_2Cl_2 (3 × 20 mL) and dried under vacuum to yield a light orange solid (0.35 g, 88%). In DMSO-d_6, both the ^{1}H and ^{13}C NMR spectra correspond to a chiral molecule and so are assigned the monosolvate structure [(tacn)RhEt(DMSO)(OTf)](OTf). ^{1}H NMR (DMSO-d_6, 360 MHz): δ 1.13 (t, J_{HH} = 8 Hz, RhCH_2CH_3), 2.06−2.20 (m, RhCH_2), 2.75−3.31 (m, NCH_2), 5.68, 6.12, 6.90 (3 br s, NH). ^{13}C{^{1}H} (DMSO-d_6, 63 MHz): δ 15.22 (d, J_{RhC} = 21 Hz, RhCH_2), 16.74 (RhCH_2CH_3), 42.70, 48.88, 49.40, 49.51, 51.44, 56.08 (5s, NCH_2). Anal. Calcd for $C_{10}H_{20}N_3F_6O_6S_2Rh$: C, 21.48; H, 3.60; N, 7.51. Found: C, 21.45; H, 2.91; N, 7.22. FAB mass spectrum from H_2O/glycerin volatilized [(tacn)-Rh(Et)(OTf)]$^+$: Calcd for [$C_9H_{20}N_3F_3O_3SRh$]$^+$, *m/e* 410.0233; found, *m/e* 410.0229 (16%) (1 ppm). Also observed, *m/e* = 382 (11%) [M^+ − C_2H_4]. Dissolution in D_2O afforded **[(tacn)RhEt(D_2O)$_2$](OTf)$_2$ (4b-d_4)**. ^{1}H NMR (D_2O, 360 MHz): δ 1.08 (t, J_{HH} = 8 Hz, RhCH_2CH_3), 2.61 (dq, J_{RhH} = 2.5 Hz, J_{HH} = 8 Hz, RhCH_2), 3.02−3.48 (m, NCH_2), 5.65 (br s, 1H, NH), 5.90 (br s, 2H, NH). ^{13}C{^{1}H} NMR (D_2O, 90 MHz): δ 12.52 (d, J_{RhC} = 23 Hz, RhCH_2), 15.78 (RhCH_2CH_3), 45.89, 51.42, 53.10 (3s, NCH_2). The downfield NH proton peak at δ 5.90 disappeared with an approximate half-time of 10 h.

(tacn)RhPh(OTf)$_2$ (3c). The procedure was the same as for **3a**, using 3.1 mL of a 0.201 N solution of HOTf (0.63 mmol) in ether and 0.15 g (0.32 mmol) of (tacn)$RhPh_3$ (**1c**) in 70 mL of CH_2Cl_2. The precipitate was washed with CH_2Cl_2 (3 × 20 mL) and dried under vacuum to yield a light orange solid (0.18 g, 92%). Anal. Calcd for $C_{14}H_{20}N_3F_6O_6S_2Rh$: C, 27.69; H, 3.32; N, 6.92. Found: C, 27.56; H, 3.17; N, 6.89. In DMSO-d_6, both the ^{1}H and ^{13}C NMR spectra correspond to a chiral molecule and so are assigned the monosolvate structure [(tacn)RhPh-

(DMSO)(OTf)](OTf). ^{1}H NMR (DMSO-d_6, 360 MHz): δ 2.24−3.54 (m, NCH_2), 3.61, 6.72 (2 br s, NH), 7.10−7.63 (m, RhC$_6H_5$ + 1NH). ^{13}C{^{1}H} NMR (DMSO-d_6, 62 MHz): δ 44.62, 49.35, 50.11 (2C), 51.93, 55.66 (5 s, NCH_2), 124.71 (Ph), 128.5 (2C, Ph), 135.19 (2C, Ph), 148.83 (d, J_{RhC} = 29 Hz, *ipso*-*C*). Dissolution in D_2O afforded **[(tacn)RhPh(D$_2$O)$_2$](OTf)$_2$** (**4c**-d_4). ^{1}H NMR (D_2O, 360 MHz): δ 2.39−3.53 (m, NCH_2), 6.04 (br s, 1H, NH), 6.26 (br s, 2H, NH), 7.25−7.50 (m, RhC$_6H_5$). The downfield NH proton peak at δ 6.26 disappeared completely within 6 h.

[(tacn)RhEt(OTf)(PMe$_3$)](OTf) (5b). PMe_3 (68 μL, 0.65 mmol) was added to a stirred solution of (tacn)RhEt(OTf)$_2$ (0.38 g, 0.62 mmol) in 40 mL of THF in a −78 °C bath. After 5 min, the mixture was allowed to warm to RT. After 20 min the mixture became cloudy, and stirring was continued for an additional 2 h. The solution was filtered, and the solvent was evaporated under vacuum to yield a yellow solid (0.36 g, 90%). In the NMR solvent DMSO-d_6, **5b** undergoes solvolysis to [(tacn)RhEt(DMSO)(PMe$_3$)](OTf)$_2$ over the period of 2 h. ^{1}H NMR (DMSO-d_6, 360 MHz, after 2 h): δ 1.06−1.10 (m, 5H, RhCH_2CH_3), 1.53 (d, J_{PH} = 11 Hz, PCH_3), 2.83−3.21 (m, NCH_2), 5.93, 6.01, 6.19 (3 br s, NH). ^{13}C{^{1}H} (DMSO-d_6, 90 MHz): δ 10.40 (dd, J_{RhC} = 7 Hz, J_{PC} = 21 Hz, RhCH_2), 13.52 (d, J_{PC} = 34 Hz, PCH_3), 16.77 (RhCH$_2$$CH_3$), 46.55, 49.70, 51.25, 53.44, 54.75, 54.80 (6 s, NCH_2). ^{31}P{^{1}H} (DMSO-d_6, 145 MHz): δ 6.08 (d, J_{RhP} = 121 Hz). Anal. Calcd for $C_{13}H_{29}N_3F_6O_6S_2PRh$: C, 24.57; H, 4.60; N, 6.61. Found: C, 24.29; H, 4.85; N, 6.54.

[(tacn)Rh(H)Me(PMe$_3$)]OTf (6a). PMe_3 (28 μL, 0.28 mmol) was added to a stirred solution of (tacn)RhMe(OTf)$_2$ (0.15 g, 0.28 mmol) in 30 mL of THF in a −78 °C bath. After 10 min the mixture was allowed to warm to RT. After the mixture was stirred for an additional 2.5 h, a small sample of the [(tacn)Rh(OTf)Me(PMe$_3$)](OTf) (**5a**) was removed for mass spectral analysis. FAB mass spectrum: Calcd for $[C_{11}H_{27}N_3F_3O_3PSRh]^+$, *m*/*e* 472.0518; found, *m*/*e* 472.0491 (100%) (6 ppm). Also observed, *m*/*e* = 457 (8%) [M$^+$ − CH_3] and 396 (78%) [M$^+$ − PMe_3]. The rest of the THF solution of **5a** was transferred by cannula to a Schlenk flask containing 15 mg of $NaBH_4$ (0.40 mmol) (or KBH_4 could be used), and this was stirred for 3 h. Some brown precipitate was removed by filtration, and the solvent was evaporated under vacuum to yield a tan solid (0.12 g), which was a 9:1 mixture of **6a** and **7** (*ca*. 90% of the two) and some residual $NaBH_4$. Spectra of the cation of **6a** in DMSO-d_6 were identical to those of **8a** given below.

[(tacn)Rh(H)Me(PMe$_3$)](BAr$^F_4$) (8a). A mixture of [(tacn)-RhMe(H)(PMe$_3$)](OTf) (80 mg, 0.17 mmol), $NaBAr^F_4$ (13 mg, 0.15 mmol), and C_6H_5Cl (15 mL) was stirred at RT for 3 h. The solution was filtered, and the solvent was removed under vacuum to yield off-white, solid **8a** (0.15 g, 75%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ −17.67 (dd, J_{RhH} = 27 Hz, J_{PH} = 36 Hz, RhH), −0.23 (dd, J_{PH} = 4.0 Hz, J_{RhH} = 2.3 Hz, RhCH_3), 1.31 (d, J_{PH} = 10 Hz, PCH_3), 2.51−3.20 (m, NCH_2), 4.92, 5.12, 5.76 (3 br s, NH). ^{13}C{^{1}H} (DMSO-d_6, 90 MHz): δ −14.34 (dd, J_{RhC} = 27 Hz, J_{PC} = 12 Hz, RhCH_3), 17.20 (d, J_{PC} = 33 Hz, PCH_3), 45.05, 46.82, 47.86, 48.74, 48.95, 49.37 (6 s, NCH_2). Anion ($^-$BAr$^F_4$) resonances: δ 117.67 (C_4), 123.98 (q, J_{FC} = 273 Hz, CF_3), 128.46 (q, J_{FC} = 30 Hz, C_3), 134.04 (C_2), 160.92 (1:1:1:1 q, J_{BC} = 49 Hz, C_1). ^{31}P{^{1}H} (DMSO-d_6, 145 MHz): δ 12.85 (d, J_{RhP} = 139 Hz). FAB mass spectrum volatilized [M$^+$ − H]: Calcd for $[C_{10}H_{27}N_3PRh]^+$, *m*/*e* 323.0998; found, 323.0996 (85%). Also observed, *m*/*e* = 308 (27%) [M$^+$ − CH_4].

[(tacn)Rh(H)Et(PMe$_3$)]OTf (6b). A mixture of THF (20 mL), [(tacn)RhEt(OTf)(PMe$_3$)](OTf) (**5b**, 0.10 g, 0.15 mmol), and $NaBH_4$ (20 mg, 0.26 mmol) (or KBH_4 could be used) was stirred at RT for 3 h. The solution was filtered, and the solvent was removed under vacuum. The solid residue was extracted with benzene (5 × 40 mL), and the benzene was removed under vacuum to yield tan, solid **6b** (48 mg, 63%). Spectra of the cation of **6b** in DMSO-d_6 were identical to those of **8b** below.

[(tacn)Rh(H)Et(PMe$_3$)][BAr$^F_4$] (8b). A mixture of [(tacn)-Rh(H)Et(PMe$_3$)](OTf) (**6b**, 18 mg, 0.034 mmol), $NaBAr^F_4$ (29 mg, 0.033 mmol), and C_6H_5Cl (15 mL) was stirred at RT for 3 h. The solution was filtered, and the solvent was removed under vacuum to yield white solid **8b** (36 mg, 90%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ −18.07 (dd, J_{RhH} = 28 Hz, J_{PH} = 36 Hz, RhH), 0.78−0.93 (m, 5H, RhCH_2CH_3), 1.34 (d, J_{PH} = 9 Hz, PCH_3), 2.58−2.80 (m, NCH_2), 4.76, 4.92, 5.54 (3 br s, NH). ^{13}C-{^{1}H} NMR (DMSO-d_6, 90 MHz): δ −0.29 (dd, J_{RhC} = 26 Hz, J_{PC} = 11 Hz, RhCH_2), 17.25 (d, J_{PC} = 32 Hz, PCH_3), 19.64 (RhCH$_2$$CH_3$), 46.18, 47.18, 48.47, 48.98, 49.91, 50.06 (NCH_2); anion resonances as in **8a** above. ^{31}P{^{1}H} (DMSO-d_6, 145 MHz): δ 12.38 (d, J_{RhP} = 145 Hz). Anal. Calcd for $C_{43}H_{42}N_3F_{24}PBRh$: C, 42.99; H, 3.52; N, 3.50. Found: C, 42.38; H, 3.16; N, 3.50. FAB mass spectrum: Calcd for $[C_{11}H_{30}N_3PRh]^+$, *m*/*e* 338.1232; found, *m*/*e* 338.1232 (11%). Also observed, *m*/*e* = 308 (36%) [M$^+$ − C_2H_6].

[(tacn)Rh(H)Ph(PMe$_3$)](OTf) (6c). Method A. [(tacn)-Rh(H)Et(PMe$_3$)]OTf (25 mg, 0.051 mmol) and 5 mL of C_6H_6 were sealed in a 9-mm, medium-walled glass tube, and the sample was heated at 80 °C for 10 h. The tube was opened, and the solution was filtered and the solvent evaporated under vacuum to yield tan, solid **6c** (24 mg, 87%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ −16.75 (dd, J_{PH} = 35 Hz, J_{RhH} = 28 Hz, RhH), 1.20 (d, J_{PH} = 10 Hz, PCH_3), 2.67−3.10 (m, NCH_2), 5.07, 5.51, 5.56 (3 br s, NH), 6.73−6.82 (m, 3H, C_6H_5), 7.34−7.36 (m, 2H, C_6H_5). ^{13}C{^{1}H} (DMSO-d_6, 90 MHz): δ 17.22 (d, J_{PC} = 34 Hz, PCH_3), 46.16, 48.13, 48.56, 49.12, 49.67, 50.22 (NCH_2), 120.86 (Ph), 126.12 (2C, Ph), 128.31 (2C, Ph), 145.87 (d, J_{RhC} = 33 Hz, Ph). ^{31}P{^{1}H} (DMSO-d_6, 145 MHz): δ 10.46 (d, J_{RhP} = 136 Hz). FAB mass spectrum: Calcd for $[C_{15}H_{30}N_3PRh]^+$, *m*/*e* 386.1232; found, 386.1227 (93%) (2 ppm). Also observed, *m*/*e* = 308 (58%) [M$^+$ − C_6H_6].

Method B. PMe_3 (20 μL, 0.20 mmol) was added to a stirred solution of (tacn)RhPh(OTf)$_2$ (**3c**) (0.12 g, 0.20 mmol) in 30 mL of THF at −78 °C. The mixture was stirred for 10 min and then allowed to warm to RT. After being stirred for an additional 2.5 h, the solution was transferred by cannula to a Schlenk flask containing 15.0 mg of $NaBH_4$ (0.40 mmol), and this was stirred for 3 h. Some brown precipitate was removed by filtration, and the solvent was removed under vacuum to yield a brown solid. The solid was extracted with C_6H_6 (3 × 40 mL), and solvent removal gave a tan solid (75 mg, 71%). Spectra were as in method A above.

[(tacn)Rh(H)$_2$PMe$_3$]X (7/9). THF (25 mL) was added to a mixture of [(tacn)RhEt(PMe$_3$)(OTf)](OTf) (**5b**, 0.10 g, 0.57 mmol) and KBH_4 (10 mg, 0.19 mmol), and the mixture was stirred at RT for 3 h. The solution was filtered, and the solvent was removed under vacuum to give a mixture of crude brown solid **7** and some **6b**. This mixture was transferred to a 9-mm, medium-walled glass tube which contained 5.0 mL of C_6H_6. The tube was sealed under vacuum and heated at 80 °C for 10 h to convert the small amount of **6b** all to **6c** which is more benzene soluble. The tube was opened, the supernatant was decanted by cannula, and the precipitate was washed with C_6H_6 (2 × 10 mL) and dried under vacuum to give tan, solid [(tacn)Rh(H)$_2$PMe$_3$](OTf) (7, 55 mg, 76%). A mixture of [(tacn)Rh(H)$_2$PMe$_3$](OTf) (55 mg, 0.12 mmol), $NaBAr^F_4$ (101 mg, 0.11 mmol), and C_6H_5Cl (15 mL) was stirred at RT for 3 h. The solution was filtered and the solvent was removed under vacuum to yield white, solid **9** (124 mg, 93%). ^{1}H NMR (DMSO-d_6, 360 MHz): δ −17.38 (dd, J_{PH} = 35 Hz, J_{RhH} = 25 Hz, RhH), 1.34 (d, J_{PH} = 10 Hz, PCH_3), 2.62−2.84 (m, NCH_2), 5.34 (br s, 2H, NH), 6.12 (br s, 1H, NH), 7.60−7.70 (br s, BAr$^F_4$). ^{13}C{^{1}H} (DMSO-d_6, 90 MHz): δ 20.78 (d, J_{PC} = 33 Hz, PCH_3), 48.60, 48.74, 49.29 (NCH_2); anion resonances as in **8a**. ^{31}P{^{1}H decoupled, RhH coupled} (DMSO-d_6, 145 MHz): δ 10.81 (dt, J_{RhP} = 131 Hz, J_{HP} = 26 Hz). Anal. Calcd for $C_{41}H_{38}N_3F_{24}PBRh$: C, 41.97; H, 3.26; N, 3.58. Found: C, 41.83; H, 3.03; N, 3.50.

CnRhEt$_3$. An ether solution of Et_2Mg (30 mL of 0.48 N, 7.2 mmol) was slowly added to a mixture of $CnRhCl_3$ (1.1 g, 2.6 mmol) and 60 mL THF at −78 °C. The cold bath was removed, and the mixture was stirred at RT for 2 h. Then 5

mL of MeOH was added to the clear yellow-brown solution to destroy excess Et_2Mg. The solvents were removed under vacuum, and the solid residue was extracted with ether (3 × 30 mL). Evaporation of the ether gave a light yellow solid (0.35 g, 37%). ^{1}H NMR (C_6D_6, 500 MHz): δ 1.22 (dq, J_{RhH} = 3.6 Hz, J_{HH} = 8 Hz, RhCH_2), 1.50 (dt, J_{RhH} = 1.8 Hz, J_{HH} = 8 Hz, RhCH$_2$CH_3), 1.56−1.63 (m, 6H, NCH_2), 2.02−2.10 (m, 6H, NCH_2), 2.21 (s, NCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 125 MHz): δ 8.40 (d, J_{RhC} = 40 Hz, RhCH_2), 16.27 (RhCH$_2$$CH_3$), 48.41 (N$CH_3$), 57.14 (N$CH_2$). DEI mass spectrum: Calcd for $[C_{15}H_{36}N_3Rh]^+$, *m/e* 361.1964; found, *m/e* 361.1962 (1.3%) (1 ppm). Also observed, *m/e* = 302 (11%), $[CnRh(C_2H_4)]^+$.

CnRhEt(OTf)$_2$. A 1.6 mL portion of a 0.651 N HOTf solution in ether (1.0 mmol) was slowly added to a stirred solution of 0.20 g (0.55 mmol) of $CnRhEt_3$ in 60 mL of CH_2Cl_2 at −78 °C. The mixture was allowed to warm and was stirred at RT for 40 min. The precipitate was collected, washed with CH_2Cl_2 (3 × 20 mL), and dried under vacuum to give light orange, solid $CnRhEt(OTf)_2$ (0.27 g, 84%). Anal. Calcd for $C_{13}H_{26}N_3F_6O_6S_2Rh$: C, 25.96; H, 4.36; N, 6.99. Found: C, 25.79; H, 4.44; N, 6.82. FAB mass spectrum from H_2O/glycerin volatilized $[CnRh(Et)(OTf)]^+$: Calcd for $[C_{12}H_{26}N_3F_3O_3SRh]^+$, *m/e* 452.0702; found, *m/e* 452.0720 (22%) (4 ppm). Also observed, *m/e* = 424 (66%) $[M^+ - C_2H_4]$.

[CnRh(H)Et(PMe$_3$)](OTf). PMe_3 (26 μL, 0.25 mmol) was added to a mixture of $CnRhEt(OTf)_2$ (0.15 g, 0.25 mmol) and 30 mL of THF at −78 °C, and the mixture was allowed to warm to RT. After the mixture was stirred for 15 min at RT, $NaBH_4$ (10 mg, 0.26 mmol) was added to the clear yellow solution, and the new mixture was stirred for 3 h. The solution was filtered, and the solvent was removed under vacuum to yield a tan solid (0.12 g, 82%). ^{1}H NMR (THF-d_8, 500 MHz): δ −19.50 (dd, J_{RhH} = 30 Hz, J_{PH} = 38 Hz, RhH), 1.10−1.26 (m, RhCH_2), 1.49 (d, J_{RhP} = 9 Hz, PCH_3), 2.69, 2.89, 2.97 (3s, NCH_3), 2.81−3.20 (m, NCH_2). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz): δ 12.50 (dd, J_{RhC} = 23 Hz, J_{PC} = 8 Hz, RhCH_2), 18.60 (d, J_{PC} = 32 Hz, PCH_3), 23.20 (RhCH$_2$$CH_3$), 51.68, 53.61, 54.63 (3s, NCH_3), 58.06, 58.15, 59.56, 59.95, 61.10, 63.25 (6s, NCH_2). ^{31}P{^{1}H} NMR (THF-d_8): δ 0.61 (d, J_{RhP} = 153 Hz, PMe$_3$).

[CnRh(H)Et(PMe$_3$)](BAr$^F_4$). A mixture of [CnRh(H)Et-(PMe$_3$)](OTf) (0.10 g, 0.19 mmol), $NaBAr^F_4$ (0.15 g, 0.17 mmol), and 25 mL of C_6H_5Cl was stirred at RT for 3 h. The solution was filtered and the solvent was removed under vacuum to yield a light brown solid (0.19 g, 90%). The NMR spectra were identical to those reported for [CnRh(H)Et(PMe$_3$)](OTf) above. FAB mass spectrum: Calcd for $[C_{14}H_{36}N_3PRh]^+$, *m/e* 380.1702; found, *m/e* 380.1710 (27%) (2 ppm). Also observed, *m/e* = 350 (100%) $[M^+ - C_2H_6]$.

Kinetics. A solution of the rhodium alkyl hydride salt, typically *ca.* 5 mg (4 μmol) in C_6D_6 in a 5-mm NMR tube, was freeze−pump−thaw degassed, and the tube was sealed. The samples were heated in an oil bath at 80 °C, and the progress of their reactions was followed by NMR at RT. Disappearance of [(tacn)Rh(H)Me(PMe$_3$)](BAr$^F_4$) (**8a**) was followed by monitoring the RhCH_3 ^{1}H NMR peak relative to the BAr$^F_4$$^-$ resonances. The reaction exhibited clean, first-order kinetics over 4 half-lives with a rate constant of 2.65(±0.02) × 10^{-5} s^{-1} and R^2 = 0.999. The conversion of [(tacn)Rh(H)Et(PMe$_3$)]-(BA$^F_4$) (**8b**) to [(tacn)Rh(D)(C$_6$D$_5$)(PMe$_3$)](BAr$^F_4$) (**8c**-d_6) was followed by ^{31}P NMR by monitoring the RhP(CH$_3$)$_3$ peaks of the reactant and product. The reaction exhibited clean, first-order kinetics over 4 half-lives with a rate constant of 1.60-(±0.03) × 10^{-4} s^{-1} and R^2 = 0.997.

X-ray Structure Determination of (tacn)RhEt$_3$ (1b). Complex **1b** was crystallized from CH_2Cl_2 as colorless blocks, and a single crystal suitable for data collection was mounted on a glass fiber in a random orientation. Selected crystallographic and refinement data are given in Table 3. Complete data are given in the Supporting Information. Three-dimensional, −100 °C X-ray data (Mo Kα radiation (λ = 0.710 73 Å), μ(Mo Kα) = 11.65 cm^{-1}, F(000) = 672) were collected in the range 2.0 < 2θ < 45° on a Syntex P4 diffractometer by the ω-scan method. The 2291 independent reflections (of 3374 measured) for which $I > 4\sigma(I)$ were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods and refined by least-squares methods. Hydrogen atoms were included in calculated positions in a riding mode. Refinement converged at a final R = 3.42 (R_w = 3.74) with allowance for the thermal anisotropy of all non-hydrogen atoms. Selected distances and angles are given in Table 1.

Table 3. Selected Crystallographic Data for 1b,c

compd	(tacn)RhEt$_3$ (**1b**)	(tacn)RhPh$_3$ (**1c**)·MeOH
empirical formula	$C_{12}H_{30}N_3Rh$	$C_{25}H_{34}N_3ORh$
color; habit	colorless, stable	pale yellow, stable
cryst size (mm)	0.50 × 0.40 × 0.50	0.40 × 0.45 × 0.50
cryst system	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a (Å)	8.244(2)	8.041(2)
b (Å)	13.143(2)	10.998(2)
c (Å)	13.462(2)	13.723(2)
α (deg)	90.00	69.17(2)
β (deg)	98.28(2)	81.02(2)
γ (deg)	90.00	85.65(2)
V (Å^3)	1443.4(5)	1120.1(4)
molecules per unit cell (Z)	4	2
fw	319.30	527.51
calcd density (g cm^{-3})	1.469	1.469
2θ(max) (deg)	45.0	45.0
reflcns collcd	3374	3545
reflcns used	2291 [$F > 4\sigma(F)$]	2749 [$F > 4\sigma(F)$]
no. of params refined	145	290
final agreement factors	$R(F)$ = 0.0342 R(wF) = 0.0374	$R(F)$ = 0.0352 R(wF) = 0.0402

X-ray Structure Determination of (tacn)RhPh$_3$·CH$_3$-OH (1c·CH$_3$OH). Complex **1c** was crystallized from CH_2Cl_2 as light yellow blocks, and a single crystal suitable for data collection was mounted on a glass fiber in a random orientation. Selected crystallographic and refinement data are given in Table 3. Complete data are given in the Supporting Information. Three-dimensional, room-temperature X-ray data (Mo Kα radiation (λ = 0.710 73 Å), μ(Mo Kα) = 7.84 cm^{-1}, F(000) = 516) were collected in the range 2.0 < 2θ < 45° on a Syntex P4 diffractometer by the ω-scan method. The 2749 independent reflections (of 3545 measured) for which $I > 4\sigma(I)$ were corrected for Lorentz and polarization effects. The structure was solved by Patterson methods and refined by least-squares methods. Methanol molecules were found partially populated in two unique positions (four per unit cell). Refinement of their populations resulted in a total content of *ca.* one solvent molecule per rhodium. Hydrogen atoms were included in calculated positions in riding mode. Refinement converged at a final R = 3.52 (R_w = 4.02) with allowance for the thermal anisotropy of all non-hydrogen atoms. Selected interatomic distances and angles are given in Table 1.

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Supporting Information Available: Complete crystallographic data for **1b**,**c**, including tables of X-ray parameters, positional and thermal parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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