Hydride and Dihydrogen Ruthenium Complexes of the Tripyrrolylphosphine Ligand

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Received February 27, 1998

The reactivity of the ruthenium(IV) trihydride complex $Cp^*RuH_3(Ppyl_3)$ (**2**), accommodating the π-accepting tripyrrolylphosphine ($Ppyl_3$), has been studied with regard to substitution and protonation reactions. Substitution of two hydrides by excess $Ppyl_3$ and CO leads to $Cp^*RuHL(Ppyl_3)$ (L = $Ppyl_3$, **3**; L = CO, **4**). The reaction with ^tBuNC leads first to the substitution of two hydrides by the ligand, but the reaction proceeds further to yield, through an unprecedented decyanation reaction, the cyano complex $Cp^*Ru(CN)(^tBuNC)(Ppyl_3)$ (**6**), which has been characterized by X-ray diffraction. Addition of $HSiMe_2Ph$ in refluxing toluene yields $Cp^*RuH_2(SiMe_2Ph)(Ppyl_3)$ (**7**), a dihydridosilylruthenium(IV) complex that has been characterized by spectroscopic data and an X-ray crystal structure. Finally, protonation of **4** yields the dihydrogen complex $[Cp^*Ru(H_2)(CO)(Ppyl_3)](BF_4)$ (**8**), which easily loses H_2 in solution and displays a very short T_1 minimum, in agreement with a low electron density on the metal.

Introduction

The chemistry of transition-metal hydride and dihydrogen complexes has considerably developed over the past few years, which resulted in the discovery of novel features of these compounds.[1] The main result is probably the demonstration of the importance of electronic factors for the existence and bonding modes of dihydrogen ligands.[1d−f] Thus, dihydrogen can be stretched, unstretched, or electrophilic (even superacidic in specific cases), according to the degree of back-donation from the metal. This has consequences both on the reactivity and on the spectroscopic properties of coordinated dihydrogen. The barrier of rotation of coordinated dihydrogen is, for example, very sensitive to back-bonding from the metal to dihydrogen.[2,3] Similarly, some transition-metal polyhydrides display very large H−H couplings in the NMR spectra due to a pairwise quantum-mechanical exchange.[4] This phenomenon is directly related to the barrier of exchange between the hydrides and is highly dependent upon the electronic properties of the metal.[5]

To modify the electron density on transition-metal polyhydride or dihydrogen complexes, different approaches have been explored, namely modification of the ligand sphere,[4c,f] addition of Lewis acidic coinage metal cations,[4d,j] or formation of dihydrogen bonds.[6] For polyhydrides displaying exchange couplings, this increase in electrophilicity of the metal resulted in a strong increase of the magnitude of exchange couplings. A problem with this approach, however, is that it is very difficult to modify the electronic properties of a complex without modifying the geometry of its coordination environment. The reverse is also true, and this has for example been made clear recently by synthesizing ruthenium dihydrogen complexes accommodating large-bite-angle diphosphines.[7] These complexes adopt a cis geometry for the hydride and dihydrogen ligands and are both electrophilic and unstable. This differs from

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S0276-7333(98)00141-1 CCC: $15.00
Publication on Web 07/31/1998

similar complexes prepared by Morris, which adopt a trans configuration and are stable.[8]

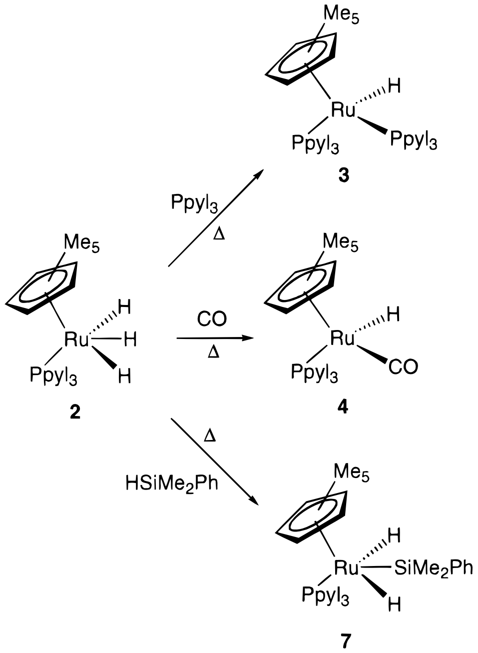
Molloy recently reported the synthesis of a new series of phosphines containing pyrrolyl substituents ($PPh_{3-x}pyl_x$, $x = 1-3$).[9] Within this series, only slight modifications of the steric properties of the phosphines were observed but a strong electronic modification, as deduced from several spectroscopic studies carried out on molybdenum and rhodium complexes.[9,10] This led us to investigate the electronic influence of this ligand on the spectroscopic properties and on the reactivity of polyhydride and dihydrogen complexes. For this purpose, we considered derivatives containing the Cp*Ru moiety. Thus, $Cp^*RuH_3(PR_3)$ was the first complex reported to exhibit quantum-mechanical exchange couplings.[4a] By a simple substitution of two hydrides, this compound leads to the monohydrides Cp*RuHLL′, which upon protonation give dihydrogen complexes.[1] Complexes of the type $[Cp^*Ru(H_2)LL']^+$ have been one of the best studied classes of dihydrogen complexes, in particular by Simpson,[11] Heinekey,[12] and Morris.[13] One particularly interesting aspect is their electrophilicity, as demonstrated by a very low pK_a.

We describe in this paper the synthesis of new ruthenium hydride and ruthenium dihydrogen complexes containing the tripyrrolylphosphine ligand, their spectroscopic properties, and some reactivity, including the formation of a dihydrido silyl complex and the decyanation of *tert*-butyl isocyanide.

Results and Discussion

The reaction of $[Cp^*RuCl_2]_n$[14] with 1 equiv of tri-*n*-pyrrolylphosphine ($Ppyl_3$) produces the ruthenium(III) complex $Cp^*RuCl_2(Ppyl_3)$ (**1**), similar to the case for other complexes accommodating different phosphines.[15] Reduction by $NaBH_4$ in ethanol affords, after appropriate treatment, the trihydride $Cp^*RuH_3(Ppyl_3)$ (**2**). **2** has been characterized by X-ray crystallography and shown to exhibit quantum-mechanical exchange couplings.[16] Whereas the crystallographic data do not significantly differ from those of $Cp^*RuH_3(PPh_3)$,[15a] the H−H coupling constants are significantly higher than those observed for $Cp^*RuH_3(PPh_3)$[17] at the same temperature, in agreement with the better π-accepting properties of the tripyrrolylphosphine ligand, which reduce the electronic density on the metal. The NMR results demonstrate that the phosphine ligand probably has a much more important effect on the thermodynamic parameters characterizing the exchange of ligands (energy difference between the ground state and the excited state, height of the barrier of exchange) than on the geometry of the ground state, shown by X-ray crystallography to be essentially similar to that of $Cp^*RuH_3(PPh_3)$. Since these thermodynamic parameters can have a strong influence on the reactivity of the complex, we studied its reactivity.

Scheme 1



The reaction of **2** with 1 equiv of $Ppyl_3$ does not proceed at room temperature, but after reflux in toluene for 6 h the monohydride complex $Cp^*RuH(Ppyl_3)_2$ (**3**) is obtained (Scheme 1). Similarly, no reaction occurs when CO is bubbled through a toluene solution of **2** at room temperature, but the hydrido carbonyl complex $Cp^*RuH(CO)(Ppyl_3)$ (**4**) is produced when the reaction is carried out in refluxing toluene for 7 h. **3** shows a sharp Ru−H stretch by infrared spectroscopy at 1972 cm^{-1}, whereas the CO stretch of **4** is observed at 1945 cm^{-1}. Both complexes were fully characterized by multinucleus NMR (see Experimental Section), the most salient feature being the presence of a high-field signal at −11.33 ppm (t, $J_{H-P} = 36.0$ Hz) and −10.50 ppm (d, $J_{H-P} = 40.7$ Hz), respectively, attributed to the hydride ligand. This reaction is relatively difficult, which suggests that no low-lying dihydrogen state facilitating the substitution reaction is present.

The same reaction is possible with ^tBuNC under the same conditions, namely refluxing toluene. The reaction occurs first similarly, and NMR monitoring in toluene-d_8 shows the presence of a complex characterized inter alia by a hydride signal at −10.99 (d, $J_{HP} = 43.1$ Hz) very similar to that of **4**, in agreement with the formulation $Cp^*RuH(^tBuNC)(Ppyl_3)$ (**5**). However, this complex transforms after 4 h into a new one which does not contain any hydride, $Cp^*Ru(CN)(^tBu\text{-}NC)(Ppyl_3)$ (**6**), and which was isolated as yellow crystals after workup of the reaction mixture. Further refluxing

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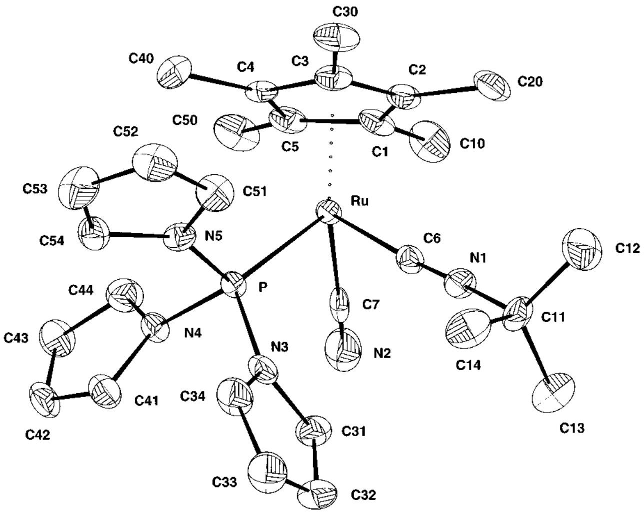

Figure 1. CAMERON view of **6**. Selected bond lengths (Å): Ru−P, 2.219(1); Ru−C(6), 1.949(6); Ru−C(7), 2.060(6); P−N(3), 1.723(5); P−N(4), 1.713(5); P−N(5), 1.702(5); C(6)−N(1), 1.155(8); C(7)−N(2), 1.103(4); N(1)−C(11), 1.453(8). Selected bond angles (deg): Ru−C(7)−N(2), 173.3(5); Ru−C(6)−N(1), 176.1(5); C(6)−N(1)-C(11), 175.0(6); P−Ru−C(7), 88.4(1); P−Ru−C(6), 88.5(2); C(6)−Ru-C(7), 93.1(2).

Table 1. Crystal Data and Data Collection Details for the Compounds $C_{28}H_{36}N_5PRu{\cdot}0.5CH_3OH$ (6) and $C_{30}H_{40}N_3SiPRu$ (7)

chem formula	$C_{28}H_{36}N_5PRu{\cdot}0.5CH_3OH$	$C_{30}H_{40}N_3SiPRu$
fw	588.68	602.80
cryst syst	monoclinic	triclinic
space group	$I2/a$	$P\bar{1}$
a (Å)	20.514(2)	9.775(1)
b (Å)	14.519(1)	11.172(2)
c (Å)	20.945(2)	14.681(2)
α (deg)	90	82.50(2)
β (deg)	93.63(1)	76.68(2)
γ (deg)	90	68.24(1)
cell vol (Å^3)	6218	1450
Z; D (g cm^{-3})	8; 1.26	2; 1.39
μ (cm^{-1})	5.69	6.49
F(000)	2429	625
cryst color	yellow	colorless
cryst size (mm)	0.45 × 0.37 × 0.13	0.50 × 0.50 × 0.40
cryst form	block	block
radiation type	Mo Kα	Mo Kα
data collecn method	ψ rotation	ψ rotation
temp (K)	180	160
no. of rflns collected	19 429	11 326
no. of rflns merged	4385	4046
R_{av}	0.064	0.04
θ_{max} (deg)	24.2	24.2

allowed the substitution of the phosphine ligand and the observation of a new complex tentatively formulated as Cp*Ru(CN)(^{t}BuNC)$_2$, in agreement with the ^{1}H NMR spectrum showing two singlets at 1.04 and 1.84 ppm for the ^{t}Bu and Cp* protons respectively in the correct integration ratio.

Table 2. Refinement Parameters for 6 and 7

compd	**6**	**7**
R^a	0.044	0.024
R_w^{b}	0.054	0.028
abs cor	none	none
weighting scheme^c	Chebyshev	none
coeff Ar	3.09, −0.471; 2.26	
goodness of fit^d	1.8	0.82
no. of rflns used	2939	4046
observn criterion	$I > \sigma(I)$	$I > \sigma(I)$
no. of params refined	327	358

[a] $R = \sum(||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = [\sum w(||F_o| - |F_c||)^2/\sum w(|F_o|)^2]^{1/2}$. [c] $w' = 1/\sum(r = 1,3)\mathrm{Ar\ Tr(X)}$, where Ar are the coefficients for the Chebyshev polynomial Tr(x) with $x = F_c/F_c(\max)$.[33] [d] Goodness of fit $= [\sum(|F_o - F_c|)^2/(N_{observus} - N_{params})]^{1/2}$.

The X-ray crystal structure of **6** carried out at 160 K demonstrated the presence of a coordinated cyano group (see Figure 1 and Tables 1 and 2). The structure displays a classical piano-stool geometry with the phosphine, the isocyanide, and the cyano groups occupying the three legs. This geometry is very similar to that recently reported for CpRu(PPh$_3$)$_2$(CN) by Kirchner *et al.*,[18] except for the Ru−C distance (2.060(6) Å) and the CN distance (1.103(4) Å), which are respectively slightly longer and slightly shorter than those of known cyanoruthenium complexes.[18,19] The Ru−C (1.949(6) Å) and CN (1.155(8) Å) distances within the coordinated isocyanide group are found in the usual range for such ligands, whereas the Ru−P distance (2.219 (1) Å) is comparable to that of **2**.

The infrared spectrum of **6** shows two strong bands at 2093 and 2137 cm^{-1} attributable to a cyano group directly attached to ruthenium and a coordinated isocyanide ligand, respectively. These two ligands are also characterized by two doublets at 134.3 ppm ($J_{C-P} = 25.3$ Hz) and 155.6 ppm ($J_{C-P} = 25.8$ Hz) in the ^{13}C NMR spectrum.

This reaction looks unusual since, to the best of our knowledge, no example of decyanation of isonitrile on transition metals has been previously reported. Reduction of isonitriles has been performed by using sodium−liquid ammonia or sodium naphthalene solutions[20] or, alternatively, by using organotin hydrides in the presence of catalytic amounts of AIBN.[21] However, the isomerization of isocyanide into nitriles is known to occur spontaneously at high temperature,[22] and a few examples of catalytic decyanation[23] and of oxidative addition of nitriles[24] to low-valent transition complexes are known. To explore this possibility, we carried out the reaction of **2** with ^{t}BuCN. However, we only observed in this case a redistribution of ligands leading quantitatively, as monitored by ^{31}P NMR, to Cp*RuH(Ppyl$_3$)$_2$ (**3**). The reaction mixture was complex, and the other phosphine free products of the reaction were not characterized. It is therefore likely that the decyanation occurs through a direct migration of the hydride onto the coordinated isocyanide ligand, leading to elimination of 2-methylpropane.

After simple substitution of two hydrides by a ligand and the observation of a novel decyanation reaction, we considered the addition of a silane to **2**. Oxidative addition or σ-Si−H coordination is very dependent upon the electronic density on the metal.[25] It was thus of

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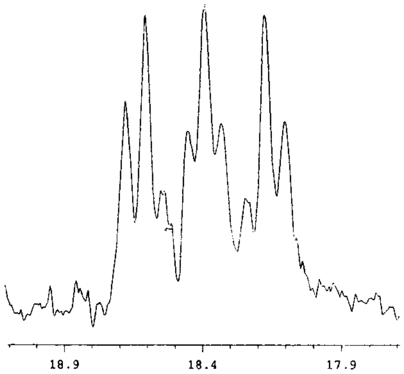

Figure 2. ^{29}Si{^{31}P}{^{1}H$_{Me}$} NMR spectrum of **7** (C_7D_8, 79.5 MHz).

interest to test the effect of the Ppyl$_3$ ligand. Addition of HSiMe$_2$Ph was carried out in refluxing toluene, yielding Cp*RuH$_2$(SiMe$_2$Ph)(Ppyl$_3$) (**7**) as a white crystalline material. The complex shows two Ru−H stretches in infrared spectroscopy at 2085 and 2055 cm^{-1}. A high-field doublet is observed at −10.41 ppm (J_{P-H} = 28.1 Hz; 400 MHz, C_7D_8) at room temperature, in agreement with the presence of two hydrides symmetrically located in the molecule around the Ru−Si bond. When the temperature is lowered, the signal broadens but no decoalescence of the signal is observed. It should be noted that Tilley et al.[26] reported the synthesis of the analogous complex Cp*RuH$_2$ (SiMePh$_2$)(PiPr$_3$) and proposed a transoid geometry for the two hydrides, whereas Caulton *et al.*[27] reported the characterization of Cp*RuH$_2$(SiR$_3$)(PiPr$_2$Ph) (R = Ph, Me, OMe) as cisoid dihydrides. These two compounds and **7** present similar ^{1}H NMR data: a doublet near −11 ppm with J_{P-H} = ca. 28 Hz. However, in the case of **7** we observed, by phosphorus decoupling, two satellites accounting for the ^{1}H−^{29}Si coupling (ca. 16 Hz). ^{29}Si NMR allows a better determination of this coupling. A singlet is observed at 18.39 ppm after ^{31}P and ^{1}H broad-band decoupling. When only ^{1}H is broad-band decoupled, a doublet is observed (J_{P-Si} = 8.8 Hz), and when a refocused INEPT experiment is carried out with selective decoupling of ^{31}P and of the methyl groups on silicon, a triplet of triplets is observed (see Figure 2, $J_{Si-H_{hydride}} = 17$ Hz; $J_{Si-H_{aromatic}} = 5$ Hz). This ^{29}Si−^{1}H coupling constant is low but is borderline between a pure two-bond coupling through the metal and a one-bond coupling in a very elongated Si−H bond.[25] A value of 22 Hz has, for example, been recently found in our group for a ruthenium complex accommodating two stretched Si−H bonds.[28] To detect any possible interaction between the silyl and hydride ligands, an X-ray crystal structure determination was carried out at 160 K. The results are shown in Figure 3 and Tables 1 and 2. **7** adopts, like **2** and **6**, a classical piano-stool structure. The Ru−P (2.2050(7) Å) and Ru−C (ca. 2.26 Å) distances are similar to those of other complexes. The Ru−H bonds are short (1.43(3) and 1.56(3) Å), in agreement with a ruthenium(IV) dihydride structure, and the Ru−Si distance (2.4213(7) Å) is in the range of reported silylruthenium complexes (mean of 2.44 Å).[26] However, the Si−H separations (1.95(3) and 2.03(3) Å) are borderline between a hydrido silyl and a η^2-silane formulation.[25,29] In summary, complex **7** is best formulated as a ruthenium(IV) dihydrido silyl derivative but, as for stretched dihydrogen complexes of rhenium and osmium in which H−H distances as high as 1.3 Å have been characterized by neutron diffraction,[30] a very weak bonding interaction between the hydrides and the silicon may be present.

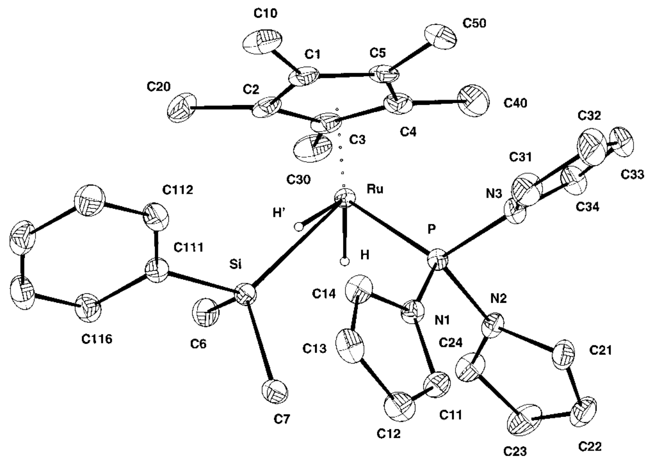

Figure 3. CAMERON view of **7**. Selected bond lengths (Å): Ru−P, 2.2050(7); Ru−Si, 2.4213(7); Ru−H, 1.43(3); Ru−H′, 1.56(3); P−N(1), 1.725(2); P−N(2), 1.717(2); P−N(3), 1.733(2); Si−C(6), 1.896(3); Si−C(7), 1.880(3); Si−C(111), 1.908(3). Selected bond angles (deg): P−Ru−Si, 100.44(2); H−Ru−H′, 104(2); P−Ru−H, 85(2); P−Ru−H′, 81(2).

As described in the Introduction, complexes of general formulation [CpRu(H$_2$)LL′]$^+$ (Cp = C$_5$H$_5$, C$_5$Me$_5$) are among the best studied families of dihydrogen complexes.[1,11−13] This led us to investigate the protonation of **2**−**4**. As for other (pentamethylcyclopentadienyl)ruthenium trihydrides, the protonation of **2** leads to loss of dihydrogen and decomposition of the complex. The protonation reactions of **3** and **4** were carried out at low temperature (195 K) directly in an NMR tube because of dihydrogen loss and extensive decomposition at room temperature. The protonation of **4** leads to the single product [Cp*-Ru(H$_2$)(CO)(Ppyl$_3$)](BF$_4$) (**8**), characterized by a broad signal at −6.15 ppm and a T_1 minimum (CD$_2$Cl$_2$, 400 MHz) of 7.9 ms at 223 K. This value is among the shortest reported for dihydrogen complexes[1] and is significantly shorter than those found for half-sandwich ruthenium complexes accommodating other phosphines.[31] In contrast with this result, in the case of the reaction of **3** with HBF$_4$·Et$_2$O, several signals were observed in the ^{1}H NMR spectrum, among which a broad signal at −6.8 ppm and a triplet at −10.6 ppm (J_{P-H} = 37 Hz), in a relative 2:1 ratio when the reaction is carried out at 193 K, can be tentatively assigned to the dihydrogen complex [Cp*Ru(H$_2$)(Ppyl$_3$)$_2$](BF$_4$) and the *trans*-dihydride isomer [Cp*Ru(H)$_2$(Ppyl$_3$)$_2$](BF$_4$), respectively. The

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two complexes display T_1 minima (C_7D_8, 250 MHz, 243 K) of respectively ca. 8 and 300 ms. Unfortunately, the compounds were found to be too unstable to be isolated and decomposed into a mixture of unidentified complexes.

Conclusion

We describe in this article the synthesis of a new series of hydride complexes containing the pentamethylcyclopentadienyl ligand (Cp*). The uniqueness of these compounds is that they contain a new electron-withdrawing phosphine ligand, tripyrrolylphosphine ($Ppyl_3$), which displays steric properties very similar to those of triphenylphosphine. This allows a direct comparison of the spectroscopic properties and of the reactivities of both series of compounds. Three products of the series have been characterized by X-ray diffraction, but only one of them (**2**) has a direct triphenylphosphine counterpart. No significant structural differences were found between both compounds and, in particular, both are formally ruthenium(IV) trihydrides. However, we found that **2** displays exchange couplings significantly higher than those of $Cp^*RuH_3(PPh_3)$.[16] This indicates the presence of a lower barrier for the classical exchange of hydrogen in the case of **2**, which is consistent with the presence of a reduced electron density on **2** compared to that on $Cp^*RuH_3(PPh_3)$. This difference is, however, presumably very small since the reactivity of **2** does not appear different from that of $Cp^*RuH_3(PPh_3)$, in particular for substitution of two hydrides by CO or $Ppyl_3$. The effect of the electron-withdrawing phosphine is also visible in the case of the dihydrido silyl compound **7** and of the dihydrogen derivative **8**. In the case of **7**, although no direct comparison with an analogous triphenylphosphine complex can be made, both the structural and the spectroscopic data suggest a very weak interaction between the hydrides and the silyl groups, even if the complex is best formulated as a ruthenium(IV) dihydride. In the case of the dihydrogen complexes, the T_1 measurements are the shortest found for this class of ruthenium compounds[1] and demonstrate the weakness of the back-bonding from the metal to dihydrogen.

In conclusion, the presence of a π-accepting ligand leads to a modification of the spectroscopic properties of ruthenium hydride complexes, in particular those related with H−H and H−Si interaction and H/H exchange. The reactivity of the complexes seems, however, little affected. We nevertheless describe a new decyanation reaction of isocyanides which has no precedent and may be due to the acidic properties of the coordinated hydrides.

Experimental Section

All manipulations were carried out with standard high-vacuum or dry argon atmosphere techniques. ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AC 200, AM 250, and AMX 400 spectrometers. The NMR chemical shifts are reported in ppm, relative to Me_4Si for ^1H and ^{13}C and relative to 85% H_3PO_4 for ^{31}P, in both cases positive in the downfield region.

$[Cp^*RuCl_2]_n$[14] and $Ppyl_3$[9] were prepared according to known methods.

Preparation of $Cp^*RuCl_2(Ppyl_3)$ (1). To a suspension of $[Cp^*RuCl_2]_n$ (600 mg, 1.95 mmol) in 20 mL of ethanol was added tri-*n*-pyrrolylphosphine (474 mg, 1.95 mmol). After 30 min of stirring, the precipitate was filtered off, washed twice with 5 mL of ethanol, and dried in vacuo. Yield: 91%. Anal. Calcd for $C_{22}H_{27}Cl_2N_3PRu$: C, 49.25; H, 5.08; N, 7.83. Found: C, 48.90; H, 4.84; N, 7.61.

Preparation of $Cp^*RuH_3(Ppyl_3)$ (2). To a suspension of $Cp^*RuCl_2(Ppyl_3)$ (229 mg, 0.4 mmol) in 10 mL of ethanol at 0 °C was added $NaBH_4$ (107 mg, 3.0 mmol). The cooling bath was removed, and the reaction mixture was stirred for 4 h at ambient temperature. After evaporation to dryness, the brown residue was extracted with 20 mL of diethyl ether. Ethanol (5 mL) was added to the filtrate, and the volume was then reduced until precipitation started. After the mixture was cooled overnight, the white crystals of $Cp^*RuH_3(Ppyl_3)$ were isolated by filtration. Yield: 82%.

IR: ν(RuH) 1978 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ −9.29 (d, J_{H-P} = 21.7 Hz, RuH), 1.73 (d, J_{H-P} = 1.9 Hz, Cp*), 6.22 (m or pseudotriplet, 6H, pyl), 6.75 (m or overlapping doublet of pseudotriplets, 6H, pyl). $^{31}P\{^1H\}$ NMR (81.02 MHz, C_6D_6): δ 129.1 (s). $^{13}C\{^1H\}$ NMR (62.89 MHz, C_6D_6): δ 10.9 (s, C_5Me_5), 98.0 (d, J_{C-P} = 3 Hz, C_5Me_5), 111.6 (d, J_{C-P} = 6.2 Hz, pyl), 123.6 (d, J_{C-P} = 6.8 Hz, pyl). Anal. Calcd for $C_{22}H_{30}N_3PRu$: C, 56.39; H, 6.47; N, 8.97. Found: C, 56.42; H, 6.53; N, 8.94.

Preparation of $Cp^*RuH(Ppyl_3)_2$ (3). To a solution of $Cp^*RuH_3(Ppyl_3)$ (200 mg, 0.43 mmol) in 10 mL of toluene was added $Ppyl_3$ (98.51 mg, 0.43 mmol). The resulting mixture was refluxed for 6 h. After evaporation to dryness, addition of 5 mL of pentane produced the precipitation of a pale yellow solid, which was filtered off, washed with pentane, and dried in vacuo. Yield: 78%.

IR: ν(RuH) 1972 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ −11.33 (t, J_{H-P} = 36.0 Hz, RuH), 1.44 (t, J_{H-P} = 1.9 Hz, Cp*), 6.14 (m or pseudotriplet, 6H, pyl), 6.59 (m or overlapping doublet of pseudotriplets, 6H, pyl). $^{31}P\{^1H\}$ NMR (81.02 MHz, C_6D_6): δ 129.0 (s). Anal. Calcd for $C_{34}H_{40}N_6P_2Ru$: C, 58.69; H, 5.81; N, 12.08. Found: C, 58.50; H, 5.94; N, 12.01.

Preparation of $Cp^*RuH(CO)(Ppyl_3)$ (4). CO was bubbled through a solution of $Cp^*RuH_3(Ppyl_3)$ (200 mg, 0.43 mmol) in 15 mL of toluene at 110 °C over 7 h. After evaporation to dryness, addition of 5 mL of pentane produced a white precipitate, which was filtered off, washed with pentane and dried in vacuo. Yield: 75%.

IR: ν(CO) 1945 cm^{-1}. ^1H NMR (200 MHz, C_6D_6): δ −10.50 (d, J_{H-P} = 40.7 Hz, RuH), 1.64 (d, J_{H-P} = 1.9 Hz, Cp*), 6.21 (m or pseudotriplet, 6H, pyl), 6.80 (m or overlapping doublet of pseudotriplets, 6H, pyl). $^{31}P\{^1H\}$ NMR (81.02 MHz, C_6D_6): δ 127.5 (s). $^{13}C\{^1H\}$ NMR (50.32 MHz, C_6D_6): δ 11.1 (s, C_5Me_5), 98.4 (s, C_5Me_5), 112.7 (d, J_{C-P} = 6.9 Hz, pyl), 124,4 (d, J_{C-P} = 8.2 Hz, pyl), 206.7 (s, CO). Anal. Calcd for $C_{23}H_{28}N_3OPRu$: C, 55.85; H, 5.72; N, 8.50. Found: C, 54.91; H, 5.54; N, 8.13.

Reaction of $Cp^*RuH_3(Ppyl_3)$ with ^tBuNC. To a solution of $Cp^*RuH_3(Ppyl_3)$ (200 mg, 0.43 mmol) in 10 mL of toluene was added ^tBuNC (97.3 μL, 0.86 mmol). The resulting mixture was refluxed for 7 h. After evaporation to dryness, addition of Et_2O/pentane (1:2) led after 2 days at −15 °C to the formation of some yellow crystals of $Cp^*Ru(CN)(t\text{-}BuNC)(Ppyl_3)$ **(6)**, which were filtered off. IR: ν(CN) 2137, 2093 cm^{-1}. ^1H NMR (200 Mz, C_6D_6): δ 0.83 (s, ^tBuNC), 1.62 (d, J_{H-P} = 2.5 Hz, Cp*), 6.21 (m or pseudotriplet, 6H, pyl), 6.94 (m or overlapping doublet of pseudotriplets, 6H, pyl). $^{31}P\{^1H\}$ NMR (81.02 MHz, C_6D_6): δ 124.3 (s). $^{13}C\{^1H\}$ NMR (100.63 MHz, C_6D_6): δ 10.5 (s, C_5Me_5), 30.8 (s, $CNCMe_3$), 57.2 (s, $CNCMe_3$), 97.0 (d, J_{C-P} = 2.8 Hz, C_5Me_5), 112.6 (d, J_{C-P} = 6.7 Hz, pyl), 124.7 (d, J_{C-P} = 7.1 Hz, pyl), 134.3 (d, J_{C-P} = 25.3 Hz, CN), 155.6 (d, J_{C-P} = 25.8 Hz, $CNCMe_3$). Anal. Calcd for $C_{28}H_{36}N_5PRu$: C, 58.51; H, 6.33; N, 12.18. Found: C, 58.83; H, 6.29; N, 11.16.

The filtrate was evaporated to dryness, and the NMR spectra show the presence of a complex characterized as Cp*RuH(^{t}BuNC)(Ppyl$_3$) **(5)**. ^{1}H NMR (200 MHz, C_6D_6): δ −10.99 (d, J_{H-P} = 43.1 Hz, RuH), 0.89 (s, ^{t}BuNC), 1.84 (d, J_{H-P} = 2.1 Hz, Cp*), 6.26 (m or pseudotriplet, 6H, pyl), 6.88 (m or overlapping doublet of pseudotriplets, 6H, pyl). ^{31}P{^{1}H} NMR (81.02 MHz, C_6D_6): δ 125.4 (s).

Preparation of Cp*RuH$_2$(Ppyl$_3$)(SiMe$_2$Ph) (7). To a solution of Cp*RuH$_3$(Ppyl$_3$) (200 mg, 0.43 mmol) in 10 mL of toluene was added SiHMe$_2$Ph (65.4 μL, 0.43 mmol). The resulting mixture was refluxed for 7 h. After evaporation to dryness, addition of 5 mL of pentane produced a white precipitate, which was filtered off, washed with pentane, and dried in vacuo. Yield: 76%.

IR: ν(RuH) 2085, 2055 cm^{-1}. ^{1}H NMR (200 MHz, C_6D_6): δ −10.63 (d, J_{H-P} = 28.1 Hz, RuH), 0.46 (s, SiMe$_2$), 1.42 (d, J_{H-P} = 2.1 Hz, Cp*), 6.22 (m or pseudotriplet, 6H, pyl), 7.03 (m or overlapping doublet of pseudotriplets, 6H, pyl), 7.22 (t, J_{H-H} = 6.6 Hz, 1 H, *p*-Ph), 7.36 (t, J_{H-H} = 7.7 Hz, 2H, *m*-Ph), 7.88 (d, J_{H-H} = 7.3 Hz, 2H, *o*-Ph). ^{31}P{^{1}H} NMR (81.02 MHz, C_6D_6): δ 136.0 (s). ^{29}Si{^{31}P} INEPT ^{1}H refocalized (79.5 MHz, C_7D_8): δ 18.39 (s). ^{29}Si INEPT ^{1}H refocalized (79.5 MHz, C_7D_8): δ 18.39 (d, J_{Si-P} = 8.8 Hz). Anal. Calcd for $C_{30}H_{40}N_3PSiRu$: C, 59.77; H, 6.70; N, 6.97. Found: C, 59.79; H, 6.76; N, 6.88.

X-ray Data for 6 and 7. For both compounds, data were collected on a Stoe Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems cooler device. The crystal-to-detector distance was 80 mm. Crystal decay was monitored by measuring 200 reflections by image. The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections, and no consequent fluctuations of the intensity were observed over the course of the data collection.

The structures were solved by direct methods (SIR92)[32] and refined by least-squares procedures on F_o. Hydrogens were located on difference Fourier maps, but they were introduced in calculations in idealized positions (d(C−H)= 0.96 Å), and their atomic coordinates were recalculated after each cycle of refinement. They were given isotropic thermal parameters 20% higher than those of the C atoms to which they were attached. In the case of **7**, the hydrides were isotropically refined. For the two compounds, all the non-hydrogen atoms were anisotropically refined except the C atoms of the solvent CH_3OH in **6**, which were isotropically refined.

Least-squares refinements were carried out by minimizing the function $\Sigma w(|F_o| - |F_c|)^2$, where F_o and F_c are the observed and calculated structure factors. A weighting scheme was used in the last refinement cycles, where weights are calculated by following the expression $w = [\text{weight}][1(\Delta(F)/6\Delta\sigma(F)]^2$.[33] Models reached a good convergence with the functions $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w(|F_o|)^2]^{1/2}$, having values listed in Table 2.

Further details of the data collection and refinement parameters are given in Tables 1 and 2. All calculations were performed with the aid of the program CRYSTALS running on a PC.[34] The drawings of the molecules were realized with CAMERON.[35]

Supporting Information is available on request from the Director of the Cambridge Crystallographic Data Center, 12 Union Road, GB−Cambridge CB2 1EZ, U.K., on quoting the full journal citation.

Protonation of Cp*RuH(CO)(Ppyl$_3$) with HBF$_4$ at Low Temperature. In a typical experiment 25 mg (0.051 mmol) of complex **3** was dissolved in 0.5 mL of CD_2Cl_2 and the solution transferred to a 5 mm NMR tube fitted with a septum. The sample was cooled to 195 K, and 9 μL of HBF$_4$·Et$_2$O (85% in Et$_2$O; 1 mmol = 173 μL) was added using a microliter syringe. The cold sample was briefly shaken to homogenize the solution and inserted into the NMR spectrometer. [Cp*Ru(H$_2$)(CO)(Ppyl$_3$)][BF$_4$] **(8)**: ^{1}H NMR (400 MHz, CD_2Cl_2, 223 K) δ −6.15 (br, Ru(η^2-H$_2$)), 1.87 (d, J_{H-P} = 2.8 Hz, Cp*), 6.47 (m, 6H, pyl), 6.59 (m, 6H, pyl); T_1(min) (400 MHz, 223 K, CD_2Cl_2) 7.9 ms.

Acknowledgment. We thank the CNRS for support. V.R. thanks the Ministerio de Educación y Cultura of Spain for a grant.

Supporting Information Available: Tables giving X-ray data for complexes **6** and **7** (14 pages). Ordering information is given on any current masthead page.

OM980141Y

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