Complexation of N_2, H_2, CO_2, and Ethylene to a T-Shaped Rhodium(I) Core

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The new rhodium−dinitrogen complex $Rh(N_2)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$ **(2)** was prepared by elimination of HCl with sodium hydride from the hydrido chloride $HRh(Cl)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$ **(1).** Complex **2** reacts with various small gaseous molecules, giving rise to the new complexes $Rh(X)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$, X = H_2 **(3)**, C_2H_4 **(4)**, CO_2 **(5)**. The first 16 electron rhodium−carbon dioxide complex **5** is spectroscopically characterized. All the transformations are reversible in the presence of free nitrogen. The thermodynamic parameters for these equilibria reactions have been evaluated. It is found that at 25 °C formation of the dihydrogen complex **3** is about 1.24 kcal/mol more favorable than formation of its dinitrogen analogue **2**, whereas formation of the carbon dioxide **(5)** and, surprisingly, ethylene **(4)** complexes is less favorable than **2** by 2.97 and 1.57 kcal/mol, respectively, yielding the ligating ability to the Rh(I) T-shaped core $L = H_2 > N_2 > C_2H_4 > (CO_2)$. The new hydrido formate $HRh(O_2CH)[HC(CH_2CH_2P(t\text{-}Bu)_2)_2]$ **(7)** can be obtained either by reaction of the dihydrogen complex **3** with CO_2 or from the carbon dioxide complex **5** with hydrogen.

Introduction

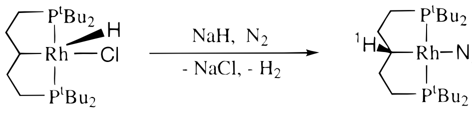
T-shaped 14 electron rhodium complexes are thought to be intermediates in a number of reactions involving Rh phosphine complexes.[1] They are normally generated by dissociation of a phosphine[2] or a carbonyl[3] ligand. In order to facilitate formation of such intermediates and also to stabilize them, we were interested in preparing square planar dinitrogen Rh(I) complexes containing a bis-chelating phosphine moiety.

Although a number of the late transition metal complexes containing a rigid P−C−P− type chelate have been reported,[4−6] such complexes containing coordinated dinitrogen are unknown. Here we describe the preparation of an alkylrhodium dinitrogen complex containing a bis-chelating phosphine system. This complex is a ready precursor to the preparation of CO_2, η^2-H_2, and ethylene complexes. We have been able, for the first time, to determine the relative stability of these four types of complexes. We found that N_2 binding competes favorably with binding of CO_2 and, surprisingly, ethylene.

Unprecedented CO_2 insertion involving a discrete dihydrogen complex is described, as well as direct hydrogenation of a novel CO_2 complex.

Results and Discussion

The dinitrogen complex **2** was obtained upon treating of the hydrido chloride **1**[7] with a large (30-fold) excess of sodium hydride in THF at room temperature for 24 h (eq 1). Although other bases are also capable of HCl removal from the metal center, sodium hydride appears to be the best since it permits the use of excess of base and the produced salt can be easily removed. $^{31}P\{^1H\}$ NMR of the crude showed only two species: the dinitrogen complex **2** (80%) and the dihydrogen complex **3** (20%). The latter is undoubtedly an intermediate in formation of **2**.



1 **2** (1)

Complex **2** is a yellow solid, highly soluble in pentane. The “end-on” bound dinitrogen can be easily identified by its characteristic stretch in the IR in the solid state (2108 cm^{-1}, film) or in solution (2117 cm^{-1}, cyclohexane). Selected NMR data of this and other complexes are summarized in Table 1.

$^{31}P\{^1H\}$ NMR exhibits a doublet at 91.50 ppm with J_{RhP} = 169.1 Hz, and in the ^1H NMR the *t*-Bu groups show two overlapping virtual triplets, which appear as two singlets in $^1H\{^{31}P\}$ NMR at 1.30 and 1.27 ppm. The ^1H-ipsoC signal is hidden under the CH_2 protons of the side chain, but it is possible to locate it at 1.85 ppm by $^{13}C-^1H$ correlation. In $^{13}C\{^1H\}$ NMR the ipso-C ap-

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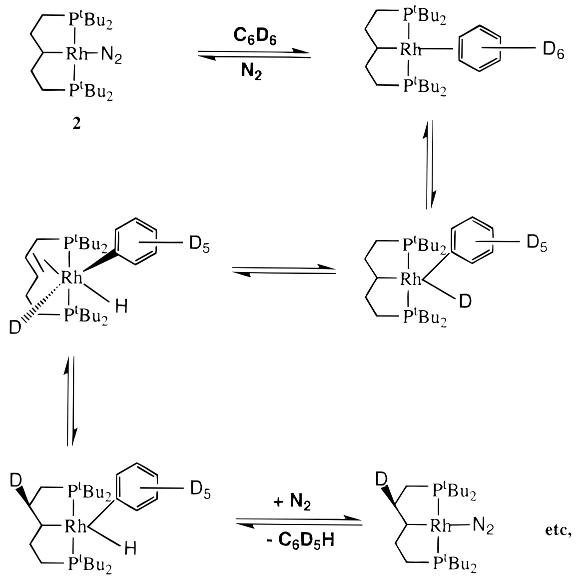
Table 1. Selected $^{31}P\{^1H\}$, ^1H, and $^{13}C\{^1H\}$ NMR Data for Complexes 2−5[a]

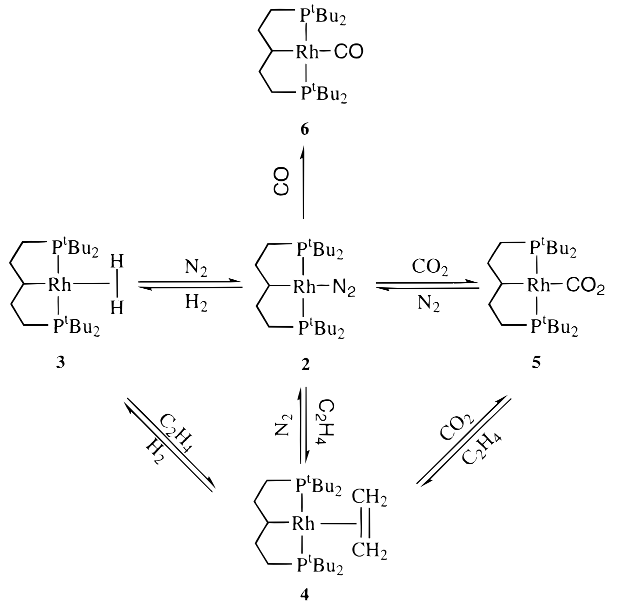
compd[b]	$^{31}P\{^1H\}$, δ (ppm) (J_{RhP}, Hz)	^1H, δ (ppm)			$^{13}C\{^1H\}$, δ (ppm)[c]		
		t-Bu	^1H-C_{ipso}	others	*t*-Bu	ipsoC_{ipso}	others
2	91.55 (169.1)	1.27 (vt), 1.30 (vt)	1.85		29.80 (vt), 29.96 (vt)	52.69 (dt, $J_{RhC} = 26.5$ Hz, $J_{PC} = 2.9$ Hz)	
3	103.62 (163.8)	1.21 (vt)		η^2-H_2, −5.0 (br hill)[d]	30.0 (vt)	59.72 (dt, $J_{RhC} = 28.4$ Hz, $J_{PC} = 2.4$ Hz)	
4	79.29 (164.5)	1.19 (m), 1.24 (m)	1.96	bound C_2H_4, 3.48 (br d)[e]	29.18 (vt), 30.71 (vt)	63.64 (dt, $J_{RhC} = 24.5$ Hz, $J_{PC} = 2.7$ Hz)	bound C_2H_4, 46.42 (br dt, $J_{RhC} = 8.0$ Hz, $J_{PC} = 1.6$ Hz)
5	80.86 (159.9)	1.20 (vt), 1.33 (vt)	0.26 (br m)[f]		29.22 (br t),[f] 20.19 (vt)	59.42 (d, $J_{RhC} = 32$ Hz)	bound CO_2, 156.0 (dt, $J_{RhC} =$ 18.4 Hz, $J_{PC} = 3.7$ Hz)

[a] A Bruker 400-MHz spectrometer was used. [b] In C_6D_6 at ca. 23 °C except where otherwise stated. [c] Abbreviations used as follows: br = broad, s = singlet, d = doublet, t = triplet, vt = virtual triplet, m = multiplet. [d] Appears as a broad singlet in toluene-d_8 at −10 °C at −6 ppm. [e] $J_{RhH} = 1.6$ Hz. [f] Toluene-d_8, −25 °C.

Scheme 1



Scheme 2



pears at 52.69 ppm as a doublet of triplets ($J_{RhC} = 26.5$ Hz, $J_{PC} = 2.9$ Hz) and the $^{13}C-^1H$ coupling constant was found to be about 130 Hz.

The dinitrogen ligand appears to be strongly bound in this crowded, electron-rich system, and the N≡N IR stretch was observed even in a coordinating solvent such as dioxane. Moreover, this apparent strong binding cannot be explained only in terms of bulkiness of the ligand system, since complex **2** is capable of coordinating larger molecules than N_2, such as arenes, as evidenced by the observed slow deuteration of the side chain when **2** is dissolved in perdeuterated aromatic solvents (benzene, toluene). It is postulated that activation of the aromatic hydrocarbons proceeds via η^2-arene intermediates[8] and, therefore, the dinitrogen ligand is capable of exchange with the arene. A possible mechanism for side chain deuteration is shown in Scheme 1.[9]

The frequency of the N≡N stretch in the IR (2108 cm^{-1}) is very close to those observed for other Rh−N_2 "end-on" bound complexes.[10] However, it is known that ν(N≡N) does not correlate well with the metal−nitrogen bond strength.[11] No changes were observed when argon was passed through a solution of **2** in benzene for 30 min. Some reactions of **2** with small molecules are shown in the Scheme 2.[12]

Reaction with CO. Upon bubbling of CO through a benzene solution of **2**, quantitative formation of **6** was observed within several seconds. All the NMR and IR data obtained are identical to those reported by Shaw et al.[7b]

Reaction of 2 with Hydrogen. Passing H_2 through a solution of **2** in benzene for several minutes results in clean formation of **3**, $^{31}P\{^1H\}$ NMR showing a new signal at 103.62 ppm (d, $J_{RhP} = 163.8$ Hz). Although complex **3** is stable for days at room temperature in solution under a hydrogen atmosphere, slow partial deuteration of the side chain occurs when **3** is left for several days in deuterated aromatic solvents. The η^2-H_2 ligand in the complex appears in ^1H NMR at room temperature as a very broad signal centered at −5 ppm.[13] Upon cooling of the sample to −10 °C, it appears as a broad singlet, but neither ^{103}Rh nor ^{31}P coupling constants are observed even at −70 °C. This cannot be explained only by a rapid rotation of the H_2 molecule around the Rh−(H_2) axis, since in the similar complex

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(8) (a) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240−4242. (b) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91−100.

(9) A C−H reductive elimination mechanism for labeling of the ipso C−H may also be operative, although we could not distinguish the ipso C−H signal from the other side chain protons.

(10) (a) Van Gaal, H. L. M.; Moers, F. G.; Steggerda, J. J. *J. Organomet. Chem.* **1974**, *65*, C43−C45. (b) Busetto, C.; D'Alfonso, A.; Maspero, F.; Perego, G.; Zazzetta, A. *J. Chem. Soc., Dalton Trans.* **1977**, 1828−1834.

(11) Deeth, R. J.; Langford, S. A. *J. Chem. Soc., Dalton Trans.* **1995**, 1−4.

(12) Complex **2** and the products of its reactions with various gases are extremely air-sensitive. Therefore, no elemental analyses based on combustion methods were performed.

(13) The chemical shift of the η^2-bound dihydrogen in ^1H NMR is usually substantially lower than those for classic hydrides. For review see: Kubas, G. *Acc. Chem. Res.* **1988**, *21*, 120−128.

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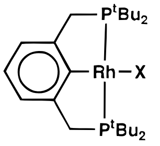
8a[6] the η^2-H_2 ligand appears as a doublet with a resolvable Rh−H coupling constant even at room temperature.



X= H_2, **8a** ; C_2H_4, **8b**

The chemical shift in ^{1}H NMR and the measured T_1 value (−40 °C, 30−60 ms), which is about 1 order of magnitude shorter than that of classical hydrides,[14] unambiguously indicate the presence of a dihydrogen species.[15] No other signals upfield from 0 ppm were observed up to −70 °C; thus, a rhodium dihydride complex (the product of oxidative addition of dihydrogen) is not detected. The protons of the *t*-Bu groups appear as a virtual triplet at 1.21 ppm (J_{PH} = 6.0 Hz), suggesting a rapid equilibrium process involving bound dihydrogen, which equilibrates the *t*-Bu groups. Moreover, the triplet of the *t*-Bu protons did not split into two different signals even when **3** was cooled down to −70 °C in toluene-d_8. In ^{13}C{^{1}H} NMR the signal of the ipso-C appears at 59.72 ppm (dt, J_{RhC} = 28.4 Hz, J_{PC} = 2.4 Hz), about 5 ppm downfield in comparison with **2**.

It is noteworthy that the position of the proton bound to the ipso-carbon atom cannot be determined. ^{13}C-{^{1}H}−^{1}H 2D correlation shows no true cross-peak for the ipso-carbon atom and *no J_{CH} coupling constant is observed* for this atom in a ^{13}C−^{1}H NMR coupled spectrum. For comparison, the same signal in complex **2** appears at 1.85 ppm with $J_{ipso\text{-}C-H}$ = 130 Hz.

The signals of the *t*-Bu groups in **3** appear to be equivalent in both ^{1}H and ^{13}C{^{1}H} NMR, a fact that can be explained only in terms of a symmetrical σ-plane passing through the rhodium atom and both phosphorus atoms. This can be a result of a rapid equilibrium process between the η^2-dihydrogen ligand and the proton of the ipso-carbon. The equilibrium is very fast even at low temperatures, as the *t*-Bu groups are equivalent even at −70 °C. Upon cooling, all the signals become broader, suggesting that the equilibrium process can be slowed down to some extent.

A similar rapid exchange was observed by Kaska et al. with an iridium(III) complex,[16] and he postulated the presence of an agostic interaction involving the metal atom and the ^{1}H-ipsoC on the basis of the lower chemical shift of this proton in comparison to the Ir(V) tetrahydride precursor and the lower ^{1}H-ipsoC coupling constant. Although, it is not completely clear whether this upfield chemical shift is due to an agostic interaction or to the difference in oxidation state of these two complexes (the difference in chemical shifts for the ipso-carbons is more than 50 ppm), in our case we also cannot rule out the possibility of involvement of an agostic interaction in the exchange between the dihydrogen ligand and the ipso-proton. We have also obtained this kind of interaction in a similar system (see below).

Complex **1** also shows fluxional behavior.[7a] The position of the hydride cannot be located by ^{1}H NMR at room temperature, and it is also impossible to find the signal of the proton bound to the ipso-carbon in ^{13}C{^{1}H}−^{1}H 2D correlation. However, the latter is observed at 2.32 ppm at low temperature (−65 °C, toluene-d_8), indicating the absence of an agostic interaction. Therefore, the presence of an agostic interaction does not seem to be an obligatory requirement for the fluxional behavior involving the proton of the ipso-carbon.

Complex **3** reacts rapidly with dinitrogen, complete conversion to **2** occurring within several minutes when **3** is exposed to a nitrogen atmosphere.

Reaction of 2 with Ethylene. The ethylene complex **4** is obtained quantitatively by bubbling ethylene through a solution of **2** in benzene for 5 min. ^{31}P{^{1}H} NMR shows a doublet at 79.29 ppm (J_{RhP} = 164.5 Hz), and in ^{1}H NMR the protons of the bound ethylene give a signal at 3.48 ppm (d, J_{RhH} = 1.6 Hz), about 2 ppm upfield from that of free ethylene. The position is also slightly shifted upfield in comparison with the similar complex **8b** (4 ppm),[6] as a result of more π-back-donation with the more electron-rich Rh complex. In ^{13}C{^{1}H} NMR, the bound C_2H_4 appears at 46.42 ppm as a broad dt (J_{RhC} = 8.0 Hz, J_{PC} = 1.6 Hz).

Substitution of the dinitrogen ligand in **2** by ethylene results in a large downfield shift of the ipso-carbon in ^{13}C{^{1}H} NMR (dt at 63.64ppm with J_{RhC} = 24.5 Hz and J_{PC} = 2.7 Hz in **4** vs 52.69 ppm in **2**), which can be explained by the higher π- acceptance capability of the ethylene ligand. The chemical shift of the proton bound to the ipso-carbon also moves downfield, although very slightly (1.95 ppm vs 1.85 in **2**).

The ethylene ligand in **4** is labile, and when exposed to a pure dinitrogen atmosphere complex, **4** is quantitatively converted into **2**. This seems remarkable considering that ethylene is a much better ligand than dinitrogen both as a σ-donor and a π-acceptor. We suppose that in the case of **4** lability of the ethylene ligand is caused mainly by the bulky environment around the rhodium atom rather than by the electronic effects. For example, no nitrogen substitution by styrene is observed even upon heating of **2** with an excess of styrene, confirming the importance of steric factors in this system.

Reaction of 2 with CO_2. Complex **2** reacts with gaseous CO_2 yielding the new Rh−CO_2 complex **5**. Examples of rhodium CO_2 complexes are extremely rare. Although their formation in various reactions has been postulated many times,[17,18] the only isolated, fully characterized rhodium CO_2 complex that we are aware of was reported by Herskovitz et al.[19] The latter complex was formulated as a saturated Rh(III) complex, bearing an η^1-CO_2^- ligand. In other cases an η^2 type of binding was suggested on the basis of IR data.[18b,c] It is

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[14] Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95−101 and references cited therein.

[15] (a) An example of a Rh(III) dihydrogen complex was reported: Bucher, U. E.; Lengweiler, T.; Nanz, D.; von Philipsborn, W.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 548−549. (b) For detailed NMR analysis see also: Nanz, D.; von Philipsborn, W.; Bucher, U. E.; Venanzi, L. M. *Magn. Res. Chem.* **1991**, *29*, S38−S44.

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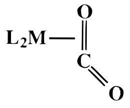
known, however, that IR data cannot be used as conclusive proof for the determination of the CO_2 binding mode.[20]

In our system formation of a “side-on” bound CO_2 is most probable. The IR spectrum shows two medium bands at 1798 and 1592 cm^{-1} (cyclohexane solution), similar to data obtained for Ni and Pd “side-on” CO_2 complexes[21,22] (**A**). The high Rh−P coupling constant



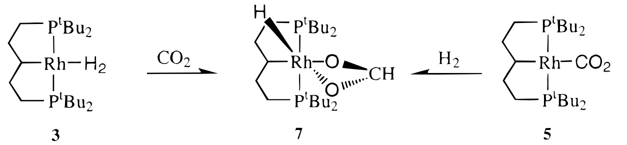
A (L= PR_3; M= Ni, Pd)

for complex **5** (80.86 ppm, d, $J_{RhP} = 159.9$ Hz) suggests that the oxidation state of rhodium in this complex is one and not three. Since the complex is relatively unstable at room temperature, most of the measurements were done at −25 °C.

$^{13}C\{^1H\}$ NMR gave a signal due to bound CO_2 at 156.0 ppm (dt, $J_{RhC} = 18.4$ Hz, $J_{PC} = 3.7$ Hz), a position that fits the “side-on” binding mode. For example, complexes **A** have chemical shifts at about 166 [22] and 159 ppm,[23] for Pd and Ni, respectively. Although we are unaware of reports of ^{13}C NMR data for Rh−CO_2 complexes, the Rh−C coupling constant seems to be very useful in analysis of the CO_2 coordination mode. It seems obvious that η^2-CO_2 complexes should have much lower Rh−C coupling constants than η^1-type complexes, and it is likely to be of a value in between that of metal−olefin and metal−alkyl (or carbonyl) complexes. In the case of **5** the Rh−C coupling constant for the CO_2 carbon is 18.4 Hz, 10.4 Hz higher than for the ethylene ligand in **4**. On the other hand, it is lower than that of Rh−alkyl (in general about 30 Hz) or carbonyl (≈50 Hz) complexes, supporting an η^2-CO_2 coordination mode in **5**. Unfortunately, the lack of information about CO_2 complexes of late transition metals in general, and rhodium in particular, does not allow us to make any generalization in the interpretation of ^{13}C NMR spectra. Nevertheless, we believe that it could be a convenient tool for the study of CO_2 coordination.[23]

Complex **5** exhibits in ^1H NMR two different virtual triplets for the protons of the *t*-Bu groups at 1.33 (J_{PH} = 6.2 Hz) and 1.20 ppm ($J_{PH} = 6.3$ Hz), and surprisingly, the ^1H-ipsoC proton appears at 0.26 ppm as a broad multiplet. We believe that such a large shift upfield compared with the starting N_2 complex (more than 1.5ppm) is a good indication for the presence of an “agostic” interaction[24] between the Rh atom and the C−H bond, providing additional stabilization of **5**. This interaction is probably promoted by the weakness of CO_2 as a ligand in comparison with nitrogen or ethylene, increasing the “unsaturated” nature of the rhodium center (see below). Interestingly, the chemical shift of the ipso-carbon in **5** is between those in **2** and **4** (it appears as a doublet in $^{13}C\{^1H\}$ NMR at 59.42 ppm, $J_{RhC} = 32.0$ Hz). Thus, variation of ligands trans to this carbon does not influence the chemical shift of this carbon in an expected way.

Scheme 3



Attempts to generate a carbene−formate species by heating of **5** at 100 °C in cyclohexane failed,[25] and only unidentified decomposition products were observed. Exposure of **5** to a N_2 atmosphere leads to the formation of **2** within several minutes.

Formation of the Hydrido−Formate 7. Complex **7** could be obtained quantitatively upon treating of **3** with CO_2 or upon reacting of H_2 with **5** at room temperature (Scheme 3). We assume that in the latter case predissociation of CO_2 takes place, followed by its insertion into the Rh−H bond.[26] Evidence for that includes the formation of a small amount of **3** when hydrogen is bubbled briskly through a solution of **5** in benzene, and therefore, CO_2 is partially being removed from the reaction solution. On the other hand, the possibility of a concerted H_2 addition to **5** cannot be excluded.[27,28] To our knowledge *this is the first demonstration of reaction of a discrete η^2-dihydrogen complex with CO_2. Reaction of a characterized CO_2 complex with H_2 to yield an insertion product is also unprecedented*. Such steps have been postulated in the process of hydrogenation of CO_2 to formic acid.[29]

The NMR data of **7** unambiguously confirm the proposed structure.[30,31] The signal of the hydride appears at −24.94 ppm as a broad singlet, and the formate proton appears as a broad doublet at 8.68 ppm, with J_{RhH} = 2.0 Hz. The position of the formate carbon (170.74 ppm, d, $J_{RhC} < 1$ Hz) is almost identical to those obtained for other metal formates. The $^{13}C-^1H$ coupled spectrum gave a very high value of $J_{HC} = 191.3$ Hz for the formate group, which is characteristic of reported formate compounds. The frequency of the Rh−H stretch in the IR at 2195 cm^{-1} is lower than that in **1** (2205 cm^{-1}), and the O−C=O absorption band appears at 1581 cm^{-1}.

The stability of **7** can be contrasted with the instability of its aromatic analogue, which could not be ob-

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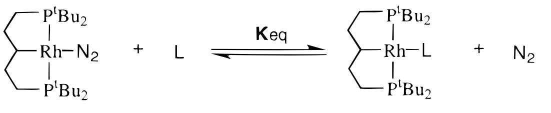
Table 2. Equilibrium Parameters for Reaction 2

incoming ligand, L	K_{eq}(298 K)	ΔG_{298}, kcal/mol
H_2	8.08 (±0.48)	−1.24 (±0.04)
C_2H_4	7×10^{-2} (±1 × 10^{-3})	+1.57 (±0.01)
CO_2	7×10^{-3} (±1 × 10^{-3})	+2.97 (±0.06)

served.[32] Lowering of the frequency of the hydride in the IR and its chemical shift in the ^1H NMR spectra as compared to **1** can be caused by the presence of one of the formate oxygen atoms trans to the hydride (in **1** this position is vacant).

Equilibria Studies. Due to the lability of the ligands bound to the Rh(I) T core in complexes **2**−**5** we were able to evaluate the relative ligating abilities of N_2, H_2, CO_2, and ethylene on the basis of equilibrium 2.



(**2**)

2

L= H_2 (**3**), C_2H_4(**4**), CO_2(**5**)

Pressurizing a solution of **2** in cyclohexane in a high-pressure 10 mm NMR tube with L/N_2 mixtures of known composition allowed the direct observation of both complexes involved in each case, and thus, the equilibrium constants could be calculated (eq 3). Solubility data for L were taken from the literature.[33] The composition of the mixture was analyzed at 25 °C at various time intervals to ensure that equilibrium has been reached, and each experiment was repeated twice with different gases ratios.

$$K_{eq} = \frac{[Rh-N_2][L]}{[Rh-L][N_2]} \tag{3}$$

The free Gibbs energies for reaction **2** are presented in Table 2.

Although many exchange reactions involving various gaseous ligands have been reported, information about the relative stabilities of the resulting complexes toward gaseous ligand dissociation is scarce. The relative stabilities of N_2 and H_2 complexes of group 6 metals (Cr, Mo, W) have been recently investigated.[34] It was noted that the stabilities of the N_2 and H_2 complexes are very close and that the preference in binding is slightly dependent on the metal. For example, in the case of Cr the dihydrogen complex is about 0.9 kcal/mol more stable than the dinitrogen one, whereas the tungsten N_2 complex is more stable than its dihydrogen analogue ($\Delta\Delta G_{298} = -0.3$ kcal/mol).

As presented in Table 2, formation of the dihydrogen complex **3** is about 1.24 kcal/mol more favorable than formation of the dinitrogen complex **2**. This is very likely to be due to higher back-bonding involving the electron-rich Rh center and the dihydrogen ligand. H_2 is known as a much better π-acceptor than dinitrogen.[35]

We were surprised to observe that dinitrogen binding (to yield complex **2**) is substantially more favorable than ethylene binding (to yield the analogous complex **4**). Despite the fact that ethylene solubility is more than 1 order of magnitude higher than that of nitrogen, both complexes **2** and **4** can be observed in a solution under equal pressure of N_2 and C_2H_4.[33b,c] The nature of this preference can be explained in terms of the bulkiness of the system. It has been very recently demonstrated[36] that the entalpy of ethylene addition to a Rh center in a less hindered system [ClRh(i-Pr$_3$P)$_2$] is about 8 kcal/mol lower than that of N_2. Although the entropy of formation for this type of complexes must also be taken into the consideration, the preference in formation of **2** over **4** represents an example of the fine tuning of the binding preferences by change of the steric demands.

As expected, formation of the CO_2 complex **5** is the least favorable for the series ($\Delta G_{298} = +2.97$ kcal/mol, reaction **2**), and therefore, the observed agostic stabilization may be essential for the existence of this species.

We are not aware of any other examples of direct comparison of stability (toward dissociation) of CO_2 and dinitrogen complexes. Moreover, here we have presented for the first time the *directly* obtained relative stabilities of metal complexes of four different gaseous ligands.

Summary

1. A new electron-rich dinitrogen rhodium complex was synthesized and spectroscopically characterized.
2. It is shown that under mild conditions nitrogen can reversibly displace ethylene, hydrogen, and CO_2 from their complexes, and the competitive binding equilibria of these ligands were determined for the first time. The stability of these complexes toward ligand dissociation follows the order $L = H_2 > N_2 > C_2H_4 > CO_2$. Substitution of nitrogen by dihydrogen causes an unusual equilibrium process involving the dihydrogen ligand and the proton of the ipso-carbon.
3. For the first time, a 16 electron rhodium−carbon dioxide complex was isolated and fully spectroscopically characterized. It is shown that the CO_2 complex **5** is stabilized by a strong agostic interaction between rhodium center and proton of the ipso-carbon. This phenomenon is observed only with the CO_2 complex and is suggested to be due to the weakness of CO_2 as a ligand in the series.
4. Unprecedented reactions of a dihydrogen complex with CO_2 and of a carbon dioxide complex with H_2 to yield a hydrido−formate complex were directly observed.

Experimental Section

General Procedures. All operations with air- and moisture-sensitive compounds were performed in a nitrogen-filled glovebox (Vacuum Atmospheres with an MO-40 purifier). All solvents were reagent grade or better. Pentane, benzene, toluene, and THF were distilled over sodium/benzophenone ketyl. All solvents were degassed and stored under high-purity nitrogen after the distillation. All deuterated solvents (Ald-

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rich) were stored under high-purity nitrogen on molecular sieves (3 Å). Sodium hydride was purchased from Merck as an 80% suspension in paraffin oil and washed with pentane in a glovebox until only traces of oil remained. All the gases were used as recieved from local sources.

^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded at 400, 162, and 100 M Hz, respectively, using a Bruker AMX400 spectrometer. All measurements were carried out in C_6D_6 or toluene-d_8 at 23 °C unless otherwise specified. ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from TMS and referenced to the residual solvent h_1 (7.15 ppm benzene, 2.10 ppm toluene) and all-d solvent peaks (128.00 ppm benzene, 20.50 ppm toluene), respectively. ^{31}P chemical shifts are in ppm downfield from H_3PO_4 and referenced to an external 85% phosphoric acid sample.

Preparation of Rh(N_2)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (2). To a solution of the rhodium hydrido chloride **1**[7a] (35 mg, 0.07 mmol) in THF (4 mL) was added 30 mg (1.25 mmol) of NaH. The suspension was vigorously stirred for 24 h at room temperature. The mixture was filtered, and THF was pumped off under vacuum. The resulting solid was dissolved in pentane. The pentane solution was filtered again to remove insoluble inorganic particles. Complex **2** was obtained as an extremely air-sensitive yellow solid after evaporation of the pentane. Yield: 31 mg (93%). *IR (film)*: 2108 cm^{-1}, s (N≡N) . *^{31}P{^{1}H} NMR (benzene-d_6, 23 °C):* 91.55 (d, J_{RhP} = 169.1 Hz). *^{1}H NMR (benzene-d_6, 23 °C):* 1.28 (two overlapped vt, appear as two singlets at 1.30 and 1.27 in ^{1}H{^{31}P} spectrum, 36H, *t*-Bu). Other signals: δ 2.03 (m), 1.88 (m), 1.45 (m). *^{13}C{^{1}H} NMR (benzene-d_6, 23 °C):* 52.69 (dt, J_{RhC} = 26.5 Hz, J_{PC} = 2.9 Hz, ipso-C). Other signals: δ 25.56 (td, J_{PC} = 8.4 Hz, J_{RhC} = 2.6 Hz, CH_2−P); 40.53 (td, J_{PC} = 9.6 Hz, J_{RhC} = 1.8 Hz, CH_2-(CH_2−P)), 36.19 (td, J_{PC} = 5.4 Hz, J_{RhC} = 1.3 Hz, C(CH_3)$_3$), 35.19 (td, J_{PC} = 6.1 Hz, J_{RhC} = 1.0 Hz, C(CH_3)$_3$), 29.96 (t, J_{PC} = 3.6 Hz, *t*-Bu CH_3), 29.8 (t, J_{PC} = 3.5 Hz, *t*-Bu CH_3).

Reaction of 2 with H_2. Formation of Rh(H_2)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (3). Dihydrogen was bubbled briskly through a solution of **2** (20 mg, 0.042 mmol) in 0.5 mL of C_6D_6 in a septum-capped NMR tube for 10 min, resulting in a color change to light-brown. NMR analysis showed disappearance of the starting material and formation of Rh(H_2)[HC(CH_2-CH_2P(*t*-Bu$_2$)$_2$] (**3**) as the only product. *^{31}P{^{1}H} NMR:* 103.62 (d, J_{RhP} = 163.8 Hz). *^{1}H NMR:* 1.21 (vt, J_{PH} = 6.0 Hz, singlet in ^{1}H{^{31}P} spectrum, 36H, *t*-Bu). Other signals: δ 2.02 (very broad s, 4H), 1.79 (broad s; t, J_{HH} = 6.5 Hz in ^{1}H{^{31}P} spectrum, 4H). H_2 bound to Rh appears as a very broad hill at −5 ppm. *^{13}C{^{1}H} NMR:* 59.72 (dt, J_{RhC} = 28.4 Hz, J_{PC} = 2.4 Hz, ipso-C). Other signals: δ 26.0 (td, J_{PC} = 7.4 Hz, J_{RhC} = 2.7 Hz, CH_2-P); 40.70 (td, J_{PC} = 9.6 Hz, J_{RhC} = 1.8 Hz, CH_2-(CH_2−P)); 34.2 (td, J_{PC} = 6.0 Hz, J_{RhC} < 0.5 Hz, C(CH_3)); 30.00 (t, J_{PC} = 3.8 Hz, *t*-Bu CH_3).

The T_1 measurements were carried out in toluene-d_8 at −40 °C. The T_1 values distributed in the 30−60 ms range.

Reaction of 2 with C_2H_4. Formation of Rh(C_2H_4)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (4). Ethylene was passed through a solution of **2** (22 mg, 0.046 mmol) in 0.5 mL of C_6D_6 in a septum-capped NMR tube for 5 min, resulting in a color change to red. NMR analysis showed disappearance of the starting material and formation of Rh(C_2H_4)[HC(CH_2CH_2P(*t*-Bu$_2$)$_2$] (**4**) as the only product. *^{31}P{^{1}H} NMR:* 79.29 (d, J_{RhP} = 164.5 Hz). *^{1}H NMR* 3.48 (broad d, J_{RhH} = 1.6 Hz, 4H, bound C_2H_4), 1.24 (m, *t*-Bu, 18H, appears as a singlet in ^{1}H{^{31}P} spectrum), 1.19 (m, *t*-Bu, 18H, appears as a singlet in ^{1}H{^{31}P} spectrum). Other signals: 2.15 (m, 2H), 2.00 (m, 3H), 1.55 (m, 4H). Signal of free ethylene: 5.24 (s). *^{13}C{^{1}H} NMR:* 63.64 (dt, J_{RhC} = 24.5 Hz, J_{PC} = 2.7 Hz, ipso-C), 46.42 (broad dt, J_{RhC} = 8.0 Hz, J_{PC} = 1.6 Hz, bound C_2H_4). Other signals: 27.35 (td, J_{PC} = 8.0 Hz, J_{RhC} = 2.1 Hz, CH_2−P), 38.92 (td, J_{PC} = 8.2 Hz, J_{RhC} = 1.6 Hz, CH_2(CH_2−P)), 36.39 (td, J_{PC} = 4.0 Hz, J_{RhC} = 1.5 Hz, C(CH_3)), 35.29 (td, J_{PC} = 4.7 Hz, J_{RhC} = 1.3 Hz, C(CH_3)), 30.71 (t, J_{PC} = 3.1 Hz, *t*-Bu CH_3), 29.18 (t, J_{PC} = 3.2 Hz, *t*-Bu CH_3). Signal of free ethylene: 122.89 (s).

Reaction of 2 with CO_2. Formation of Rh(CO_2)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (5). CO_2 was bubbled through a solution of **2** (33 mg, 0.069 mmol) in 0.5 mL of C_6D_6 in a septum-capped NMR tube for 5 min. NMR analysis showed disappearance of the starting material and formation of Rh(CO_2)[HC(CH_2-CH_2P(*t*-Bu$_2$)$_2$] (**5**) as the only product. *^{31}P{^{1}H} NMR* 80.86 (J_{RhP} = 159.9 Hz). *^{1}H NMR: (toluene-d_8, −25 °C):* 1.33 (vt, *t*-Bu, J_{PH} = 6.2 Hz, 18H, appears as a singlet in ^{1}H{^{31}P} spectrum), 1.2 (vt, *t*-Bu, J_{PH} = 6.3 Hz, 18H, appears as a singlet in ^{1}H{^{31}P} spectrum), 0.26 (br m, *H*C(CH_2−CH_2−P), 1H). Other signals: 1.68 (m, 4H), 1.48 (m, 2H). *^{13}C{^{1}H} NMR (toluene-d_8, −25 °C)*: 59.42 (d, J_{RhC} = 32.0 Hz, ipso-C), 156.00 (dt, J_{RhC} = 18.4 Hz, J_{PC} = 3.7 Hz, bound CO_2). Other signals: 22.41 (td, J_{PC} = 8.6 Hz, J_{RhC} = 2.2 Hz, CH_2−P), 40.54 (td, J_{PC} = 8.1 Hz, J_{RhC} = 2.6 Hz, CH_2(CH_2−P)), 36.66 (td, J_{PC} = 6.5 Hz, J_{RhC} = 2.0 Hz, C(CH_3)), 34.86 (t, J_{PC} = 6.4 Hz, C(CH_3)), 30.19 (t, J_{PC} = 3.4 Hz, *t*-Bu CH_3), 29.22 (br t, *t*-Bu CH_3).

Reversible Formation of 3 and 5 from 4. Bubbling of H_2 and CO_2 through a benzene solution of **4** for 10 min results in quantitative formation of **3** and **5**, respectively. The reactions are reversible upon bubbling of ethylene.

Reaction of 2 with CO. Formation of Rh(CO)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (6). CO was passed through a solution of **2** in benzene for 1 min. The quantitative formation of **6** was confirmed by ^{31}P{^{1}H} and ^{1}H NMR and IR.[7b]

Preparation of Rh(H)(η^2-O_2CH)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (7). Method A. CO_2 was bubbled through a solution of **2** (20 mg, 0.042 mmol) in 0.5 mL of C_6D_6 in a septum-capped NMR tube for 10 min. *^{31}P{^{1}H} NMR (23 °C)* analysis showed disappearance of the starting N_2 complex and formation of the CO_2 adduct **5**. Bubbling of dihydrogen through the adduct solution for 5 min and NMR analysis of the resulting solution showed disappearance of the CO_2 complex and formation of Rh(H)(η^2-O_2CH)[HC(CH_2CH_2P(*t*-Bu)$_2$)$_2$] (**7**) as the only product. *IR (film):* 2195 cm^{-1}, w (RhH), 1581 cm^{-1}, s (CO_2). *^{31}P{^{1}H} NMR:* 88.58 (d, J_{RhP} = 125.8 Hz). *^{1}H NMR:* −24.94 (very broad s, hydride, 1H), 8.68 (broad d, J_{RhH} = 2.0 Hz, O_2CH, 1H), 1.30 (vt, J_{PH} = 6.1 Hz, appears as a singlet in ^{1}H{^{31}P} spectrum, 36H, *t*-Bu). *^{13}C{^{1}H} NMR:* 170.74 (broad d, J_{RhC} < 1 Hz, O_2CH. ^{1}H-coupled spectrum showed J_{HC} = 191.3 Hz), 41.77 (d, J_{RhC} = 26.2 Hz, ipso-C). Other signals: 23.42 (td, J_{PC} = 9.5 Hz, J_{RhC} = 2.5 Hz, CH_2−P); 43.12 (td, J_{PC} = 7.4 Hz, J_{RhC} = 1.6 Hz, CH_2(CH_2−P)); 35.56 (td, J_{PC} = 7.3 Hz, J_{RhC} < 1 Hz, C(CH_3)); 29.7 (very broad hill, *t*-Bu CH_3).

Method B. CO_2 was passed through a solution of **3** in benzene (generated *in situ* from 20 mg, 0.042 mmol, of **2** in 0.5 mL of C_6D_6 and hydrogen) for 5 min. Complex **7** was obtained in a quantitative yield (see method A).

Equilibria Study. The equilibria measurments were performed in a 10 mm high-pressure NMR tube. In a typical experiment a 2:1 mixture of N_2 and hydrogen was prepared in a 100 cm^3 Fischer-Porter glass reactor at 60 psi, and it was introduced into the 10 mm high-pressure NMR tube (Wilmad 513−7PVH), containing 1.2 mL of a 0.012 M solution of **2** in cyclohexane (the total pressure decrease was taken into the consideration). The ratio between the products was monitored by ^{31}P{^{1}H} NMR at 25 °C, and the equilibrium conditions were usually achieved after 5−6 h. Solubility data of the gases were taken from the literature.[33]

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