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Note

Oxidative Addition of N–H Bonds to a Metal Center: Synthesis, Characterization, and Crystal Structure of New Rhodium(III) Hydrido–Pyrazolate Complexes

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Introduction

Catalytic and stoichiometric alkene hydroamination, which constitutes the formal addition of a N−H fragment to a carbon−carbon multiple bond, is a significant application of organometallic chemistry, aiming to obtain products of central synthetic relevance.[1] In such reactions, two alternative mechanisms are conceivable: (i) activation of the olefin through coordination, followed by nucleophilic attack of the amine, or (ii) oxidative addition of the N−H bond of the amine and subsequent insertion of the olefin into the metal−nitrogen bond. The activation of the N−H bond probably represents the most important step in the case of low-valent metal centers.[2] Unfortunately, general methods for carrying out catalytic hydroamination reactions are not yet available, and only for the hydroamination of norbornene (catalyzed by an iridium(I) complex) has the intermediate species derived from the intermolecular reaction been fully characterized.[3] This catalytic cycle has been proposed to proceed via activation of amine through N−H oxidative addition to the iridium(I) center of $Ir(PEt_3)_2Cl$, yielding a five-coordinate hydrido−amido intermediate, followed by the insertion of the olefin into the newly formed iridium−nitrogen bond.[3]

While the oxidative addition of N−H bonds of primary or secondary amines has been reported,[2,4] examples of structurally characterized hydride−amido complexes obtained in this way are rather limited.[5] A few more reports on the oxidative addition of more acidic, thus *activated*, N−H bonds (e.g., heterocycles, imides) have appeared.[5,6]

Our continuing interest in the coordination chemistry of pyrazole and related molecules has prompted us to explore the feasibility of the oxidative addition of the N−H bonds of these ligands to a metal center. In this paper we report our preliminary results on the subject, with particular emphasis on the formation of bishydridorhodium(III) species.

Results and Discussion

The mononuclear hydrido complex $[Rh(PPh_3)_4H]$[7] reacts with a stoichiometric amount of 3,5-dicarbomethoxypyrazole (Hdcmpz) in toluene at room temperature, leading to the new rhodium(III) complex $[Rh(PPh_3)_2(dcmpz)(H)_2]$, **1**, derived from the oxidative addition of the pyrazole N−H bond to the Rh(I) center:

$$[Rh(PPh_3)_4H] + Hdcmpz \rightarrow [Rh(PPh_3)_2(dcmpz)(H)_2] + 2PPh_3 \quad (1)$$

Analogously to previously reported reactions with carboxylic acids[8] and thiols,[9] we observed the oxidative addition of N−H to the Rh(I) metal center, and not dihydrogen elimination, with the corresponding formation of a rhodium(I) pyrazolate complex.

The formulation of **1** has been suggested by IR and NMR spectroscopy. Indeed, the infrared spectrum of **1** shows two sharp bands of medium intensity at 2066 and 2140 cm^{-1} attributable to the stretching of Rh−H bonds. Furthermore,

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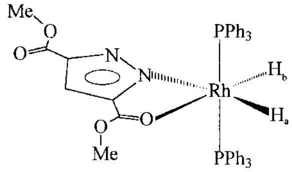
Chart 1. Schematic Drawing of Complex **1** and Significant NMR Parameters



proton	Chemical Shift (ppm)	Coupling Costants (Hz)		
H_a	-14.86	12.13 $J(H_a,H_b)$	15.99 $J(H_a, Rh)$	25.86 $J(H_b,Rh)$
H_b	-19.74		13.77 $J(H_a, P)$	15.06 $J(H_b, P)$

two other bands are present in the typical “organic” carbonyl region, and are assignable to nonequivalent COOMe groups present on the pyrazolate ligand. The first one (centered at 1700 cm^{-1}) has been associated with a COOMe group not coordinating the metal center. On the contrary, the lower frequency of the second absorption (1624 cm^{-1}) suggests a strong interaction between the oxygen of the carbonyl group and the rhodium(III) metal center. Such a chelating N,O coordination mode of the dcmpz ligand has already been observed and reported by us in the $[Cu_3(dcmpz)_6]$ and $[Cu(py)_2(dcmpz)_2]$ copper(II) compounds, with similar IR spectral features.[10]

Further information on the formulation of **1** has also been obtained by ^{31}P NMR spectroscopy. Indeed, the ^{31}P NMR spectrum of **1** shows only a doublet centered at 42.7 ppm, with spectral features not changing on lowering the temperature to 198 K. The $^{1}J(Rh,P)$ coupling constant of 119.6 Hz is typical for rhodium(III) species.[8,9] On the basis of these spectral observations and taking into account analytical data, the presence of two molecules of magnetically equivalent PPh_3 ligands coordinated to the metal center is implicit.

The ^{1}H NMR spectrum of **1** recorded in toluene-d_8 at 193 K shows, besides the signals due to aromatic protons, two singlets (1:1 ratio) centered at 2.96 and 3.73 ppm attributable to $COOCH_3$ substituents of the pyrazolate ring. In addition, two high-field multiplets, a quintet and a sextet, centered at −14.9 and −19.7 ppm, respectively, assignable to two magnetically unequivalent hydrides are also present. To accurately determine the $^{2}J(H,H)$, $^{1}J(H,Rh)$, and $^{2}J(H,P)$ coupling constants, the simulation of the hydride zone of the recorded ^{1}H NMR spectrum of **1** has been performed. Chart 1 reports the spectral parameters. The first multiplet (centered at −14.9 ppm, H_a proton) is a *pseudo*quintet thanks to the similarity between the $^{1}J(H_a,Rh)$ and $^{2}J(H_a,P)$ values. The second proton (at −19.7 ppm, H_b label) shows a $^{1}J(H_b,Rh)$ value larger than the $^{2}J(H_b,P)$ value, thus leading to a sextet. The latter can be associated with the hydride trans to the oxygen atom of the coordinated COOMe group. In fact, the Rh−O bond in **1** is presumably weaker than the Rh−N bond, giving rise to a strengthening of the Rh−H bond trans to it, with a consequent increase of the value of the $J(Rh,H)$ coupling constant and an upfield shift of the signal.

In agreement with the spectroscopic data, we suggest for species **1** a *pseudo*octahedral geometry of idealized C_s symmetry (see Chart 1) with a rhodium(III) center bound to two triphenylphosphines that take up the axial positions (in agreement with ^{31}P NMR data and particularly with the $^{2}J(H,P)$ values, typical of couplings between cis ^{1}H and ^{31}P nuclei in ligands which are about 90° from each other),[11] two mutually cis hydrogens, and one pyrazolate ligand coordinating to the metal center in the aforementioned N,O fashion.

The considerable interest in N−H bond activation and the results obtained employing Hdcmpz prompted us to further explore this reaction, with the aim to extend it to other differently substituted pyrazoles.

Consequently, we have found that the hydrido species $[Rh(PPh_3)_4H]$ easily reacts also with pyrazole (Hpz) and 3,5-dimethyl-4-nitro-pyrazole (Hdmnpz), affording two new rhodium(III) complexes, formulated as $[Rh(PPh_3)_2(pz)(Hpz)(H)_2]$, **2**, and $[Rh(PPh_3)_2(dmnpz)(Hdmnpz)(H)_2]$, **3**, in agreement with analytical and spectroscopic data:

$$[Rh(PPh_3)_4H] + 2Hpz^* \rightarrow [Rh(PPh_3)_2(pz^*)(Hpz^*)(H)_2] + 2PPh_3 \quad (2)$$

(Hpz* = pyrazole, **2**; 3,5-dimethyl-4-nitropyrazole, **3**)

The infrared spectra of species **2** and **3** show two typical absorptions of medium intensity, at 2097 and 2017 cm^{-1} for **2** and 2110 and 2050 cm^{-1} for **3**, due to the stretching of M−H bonds. In the same region, and partially overlapped with the hydride bands, an additional broad band centered at about 2050 cm^{-1} is present in both species.

It is well-known that the latter absorptions are due to strong hydrogen bonds, and are frequently found in complexes containing both pyrazole and pyrazolate ligands in sterically favorable environments,[12] as in the dimeric 3,5-dimethyl-pyrazolate (dmpz) derivatives $Zn_2(Hdmpz)_2(dmpz)_4$,[13] $Co_2(Hdmpz)_2(dmpz)_4$,[14] and $Pd_2(Hdmpz)_4(dmpz)_4$[15] or in the mononuclear rhenium(I) $[Re(CO)_3(Hpz)(pz)(py)]$ species.[16]

The presence of strong N−H···N interactions is also evident in NMR measurements. Indeed, the ^{1}H NMR spectra of both complexes, recorded in toluene-d_8 at room temperature, show, besides the signals due to the heterocyclic and phosphine ligands, a high-field multiplet (centered at −15.27 ppm for **2** and −15.87 ppm for **3**) attributable to the H(Rh) hydridic protons, and a sharp low-field singlet (centered at

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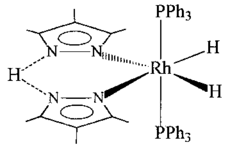
Chart 2. Schematic Drawing of Complexes **2** and **3** and Significant NMR Parameters



Coupling Costants (Hz)	Complex 2	Complex 3
	δ(H): -15.25 ppm	δ(H): -15.88 ppm
J(H, H)	0	0
$J(^1H,^{31}P)$	14.29	13.28
$J(^1H,^{103}Rh)$	16.64	16.32
T_1 (ms)	467	492

19.15 and 20.32 ppm for compounds **2** and **3**, respectively), ascribed to the N−H protons involved in the hydrogen bonds. The remarkable downfield shift of the latter signals supports the presence of fairly strong N−H−N hydrogen bonds. This type of interaction, recently defined as a *quasisymmetric hydrogen bond*,[17] is a special type of hydrogen bond in which the proton is equally shared by two atoms, that is, the forces on H from each donor atom are equal. Species containing proton-shared hydrogen bonds were found to have similar chemical shifts of about 20 ppm for the hydrogen-bonded proton, independently of the donor atoms.[17] Consistently, an X-ray study carried out on complex **3** (see below) revealed the presence of pyrazole/pyrazolate units linked by N−H···N bridges so as to formally generate a single chelating ligand of idealized C_{2v} symmetry.

The ^{31}P NMR spectra of complexes **2** and **3** show, in both cases, sharp doublets centered at 47.7 and 48.4 ppm, respectively (^1J(Rh,P) = 116.2 Hz for species **2** and 114.8 Hz for species **3**). It follows that, in complexes **2** and **3**, the two triphenylphosphines coordinating the rhodium(III) center are magnetically equivalent, as observed for complex **1**. Moreover, the aforementioned *intra*molecular hydrogen bond between the pyrazole and pyrazolato rings, and the equivalence of the two coordinated nitrogen atoms, remarkably simplifies the ^1H NMR spectra of **2** and **3**. Thus, the hydride resonances of the ^1H NMR spectra of **2** and **3** appear in both cases, thanks to the similarity between the ^1J(H,Rh) and ^2J(H,P) values, as quartets (Chart 2).

In agreement with NMR and analytical data, it is easy to suggest, for species **2** and **3,** an octahedral geometry around the rhodium(III) center, with two triphenylphosphine ligands in *axial* positions, two mutually cis hydrides, and a hydrogen-bond-stabilized pz−H−pz ligand completing the coordination sphere. Moreover, a measure of the spin−lattice relaxation times (T_1) of the hydridic protons (Chart 2) excludes the presence of interactions leading to nonclassic dihydride or molecular hydrogen complexes.[18] A detailed single-crystal X-ray diffraction study confirmed the structure for **3** proposed above.

It is worth noting that oxidative addition of the N−H bond has not been observed with substituted pyrazoles more basic than Hpz, such as 3,5-dimethylpyrazole and 3,4,5-trimethylpyrazole. That steric effects are also at work has been proven by observing that no reaction occurs by employing the bulky 3,5-diphenylpyrazole, slightly more acidic than pyrazole.

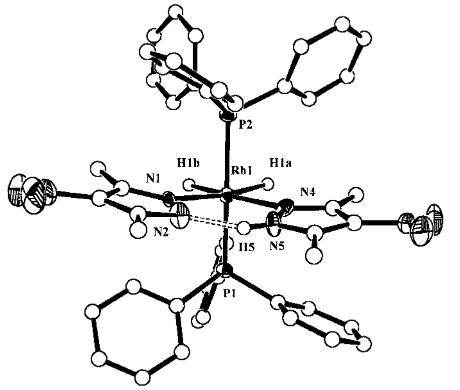


Figure 1. ORTEP drawing of the solid-state structure of $[Rh(PPh_3)_2(dmnpz)(Hdmnpz)(H)_2]$ (molecule a), with the partial labeling scheme. Empty circles indicate H and C atoms. C-bonded hydrogen atoms are omitted for clarity. Relevant bond distances (Å) and angles (deg), with esd's in parentheses, are Rh1−P1 = 2.309(3), Rh1−P2 = 2.330(3), Rh1−N1 = 2.210(8), = Rh1−N4 = 2.228(9), N2···N5 = 2.55, P1−Rh1−P2 = 167.6(1), and N1−Rh1−N4 = 93.3(4). H1a, H1b, and H5 are positioned in idealized locations. The other crystallographically independent molecule (b) is practically identical, as witnessed by the following geometric values: Rh2−P3 = 2.299(3); Rh2−P4 = 2.321(3); Rh2−N7 = 2.205(10); Rh2−N10 = 2.225(9); N8···N11 = 2.58; P3−Rh2−P4 = 167.4(1); N7−Rh2−N10 = 94.3(4).

Crystal and Molecular Structure of 3. Crystals of **3** contain two crystallographically independent molecules of $[Rh(PPh_3)_2(dmnpz)(Hdmnpz)(H)_2]$ of idealized C_{2v} symmetry, with practically identical geometric parameters. Figure 1 contains a sketch of molecule a, which is also representative of the stereochemistry of molecule b. The octahedral coordination at the Rh(III) atoms is achieved by two *trans*-PPh_3 ligands,[19] one cis chelating ligand (dmnpz−H−dmnpz, with an N−Rh−N angle of ca. 94°), and two hydrides, trans to the Rh−N vectors, which have been inserted in an idealized location (see below). Thus, the most relevant structural feature of **3** is the presence of the strongly hydrogen-bonded pyrazolate "dimer", with an acidic proton rather inert toward H_2 elimination. Whether such a bond contains a statistically disordered, or dynamically shared, H atom, or the depth of the *single*- or *double-well* potential of such an interaction, is still a matter of debate, given that independent evidence (^{15}N CP-MAS NMR,[20] neutron diffraction,[21] and theoretical studies[22]) on a number of differently substituted pyrazoles has manifested the presence of one type, or the other, of these extreme situations.[23]

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(19) With an average Rh−P distance of 2.31 Å and P−Rh−P angles near 167.5°, practically identical with the values observed in the $[Rh(PPh_3)_2(L)(H)_2]^+$ analogue (L = 3,6-bis(2′-pyridyl)pyridazine), discussed in Ghedini, M.; Neve, F.; Lanfredi, A. M. M.; Uguzzoli, F. *Inorg. Chim. Acta* **1988**, *147*, 243.

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Such a dmnpz−H−dmnpz ligand belongs to the recently discussed[24] family of H-bonded diazolates, which, depending on the torsion angle about the N−H···N hinge and on the nature of the aromatic rings involved, may bridge atoms which are 3.7 to ca. 10 Å apart (dmpz−H−dmpz in the molecular $Pd_2(Hdmpz)_4(dmpz)_4$ species,[15] and im−H−im in $M(Him)_2(im)_2$ polymers;[24] M = Pd, Pt; Him = imidazolate) or even act as chelates, as in **3**, $[Re(CO)_3(Hpz)(pz)(py)]$,[16] $Zn_2(Hdmpz)_2(dmpz)_4$,[13] and $Co_2(Hdmpz)_2(dmpz)_4$.[14]

Conclusions

The synthesis and structural properties of new dihydrido−pyrazolate complexes have been presented. The reactions discussed in this paper show that facile oxidative additions of N−H bonds of substituted pyrazoles to the rhodium(I) metal center of $[Rh(PPh_3)_4H]$ can occur. Further investigation on related systems, with the aim to extend this reactivity to more *classic* (nonactivated) primary or secondary amines, is in progress.

Experimental Section

General Procedure. Solvents were dried and purified by standard methods. All chemicals were used as supplied from Aldrich. $[Rh(PPh_3)_4H]$ was prepared according to literature procedures.[7] NMR spectra were acquired on a Bruker spectrometer operating at 300 MHz, and the infrared spectra were recorded on a Bio-Rad FTIR 7 instrument. Elemental analyses (C, H, N) were carried out at the Microanalytical Laboratory of the University of Milan. All reactions were carried out employing standard Schlenk glassware under an atmosphere of dry nitrogen. ^1H NMR simulations were performed employing the P.H.M. Budzelaar gNMR V4.01 package, Cherwell Scientific Publishing, Oxford, U.K.

$[Rh(PPh_3)_2(dcmpz)(H)_2]$, 1. A suspension of $[Rh(PPh_3)_4H]$ (0.15 g, 0.13 mmol) in oxygen-free toluene (6 mL) was kept under stirring at room temperature for 10 min. After this time, Hdcmpz (0.036 g, 0.196 mmol; Rh:Hdcmpz ratio 1:1.5) was added to the mixture under nitrogen. The orange suspension slowly became a pale orange solution. The solvent was then removed under reduced pressure, and the yellow solid was treated with diethyl ether to give a white complex, **1**, which was filtered off, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{43}H_{39}N_2O_4P_2Rh$: C, 63.55; H, 4.84; N, 3.45. Found: C, 63.1; H, 4.7; N, 3.1.

$[Rh(PPh_3)_2(Hpz)(pz)(H)_2]$, 2. A suspension of $[Rh(PPh_3)_4H]$ (0.30 g, 0.26 mmol) in toluene (5 mL) was left under stirring at room temperature for 10 min. Hpz (0.036 g, 0.52 mmol; Hdpz:Rh ratio 2:1) was then added, and the suspension was kept under stirring for 3 h. Toluene was then removed under vacuum and the residue treated with diethyl ether. The white complex was then filtered off, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{42}H_{39}N_4P_2Rh$: C, 65.97; H, 5.14; N, 7.33. Found: C,65.87; H, 5.28; N, 7.25.

$[Rh(PPh_3)_2(Hdmnpz)(dmnpz)(H)_2]$, 3. A suspension of $[Rh(PPh_3)_4H]$ (0.15 g, 0.13 mmol) in toluene (4 mL) was left under stirring at room temperature for 10 min. Hdmnpz (0.037 g, 0.26 mmol; Hdmnpz/Rh ratio 2:1) was then added, and the suspension was kept under stirring for 3 h. The white complex was filtered off, washed with diethyl ether, and dried under vacuum. Anal. Calcd for $C_{46}H_{45}N_6O_4P_2Rh$: C, 60.66; H, 4.98; N, 9.23. Found: C, 60.53; H, 4.83; N, 9.07. Crystals suitable for the X-ray structure determination were obtained by slow diffusion of diethyl ether into a toluene solution of complex **3**.

Table 1. Summary of Crystal Data and Structure Refinement Parameters for **3**

empirical formula	$C_{46}H_{45}N_6O_4P_2Rh$
fw	910.73
cryst syst	orthorhombic
space group	$Pbn2_1$
a, Å	12.537(2)
b, Å	18.113(3)
c, Å	38.231(6)
V, Å^3	8682(2)
Z	8
$F(000)$	3760
density(calcd), g cm^{-3}	1.394
temp, K	293(2)
diffractometer	Bruker SMART CCD
radiation(graph monochr), Å	0.71073
abs coeff, mm^{-1}	0.52
cryst size, mm	0.26 × 0.14 × 0.05
scan method	ω
scan interval, deg	0.3
no. of frames collected	1250
max time per frame, s	40
reciprocal space measd	hemisphere
θ range, deg	$2\theta < 50$
index ranges	$-13 \le h \le 14, -21 \le k \le 18, -43 \le l \le 39$
no. of reflns collected	34048
no. of independent obsd reflns	6752 [R(int) = 0.043]
cryst decay, %	none
abs correction	none
refinement method[a]	full-matrix least-squares on F_o^2
obsd refln criterion	$F_o > 3.0\sigma(F_o)$
absolute structure param	0.33(4)
no. of data/restraints/params	6752/1/1064
goodness-of-fit on F_o^2	1.12
final R indices	R1 = 0.047, wR2(F^2) = 0.089
largest diff peak and hole, e Å^{-3}	0.71 and −0.41

[a] Weights during refinement were $w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.4758P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Crystallography. A suitable crystal of dimensions 0.26 × 0.14 × 0.05 mm was glued to a tip of a glass fiber positioned on a goniometric head. Intensity data were collected for 34048 reflections having $2\theta < 50°$, using Mo Kα radiation, on a Bruker SMART CCD diffractometer. Crystal and intensity data are given in Table 1. The structure was solved by SIR97,[25] completed by difference Fourier, and refined by full-matrix least-squares methods with the SHELX97 program.[26] All non-H atoms were refined anisotropically to R and R_w values of 0.047 and 0.089 (6752 unique observed reflections). Hydrogen atoms, riding on their parent C atoms, were included in the final stages of the refinement in ideal positions, together with disordered H atoms, linking the “free” ends of the pyrazolate moieties. In the last difference Fourier maps, four clearly distinguishable electron density peaks (in the 0.49−0.32 e/Å^3 range) could be observed, nearly trans to the four Rh−N vectors, at distances in the 1.1−1.9 Å range. However, upon attempting their refinement, implausible thermal factors and, particularly, very bad H atom locations were obtained; therefore, we preferred to neglect their contribution and to idealize their positions as depicted in Figure 1.[27] Notwithstanding stereochemical considerations, NMR evidence

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clearly agrees with the structure proposed here. The handness of the crystal has been tested by refining two (barely distinguishable) enantiomorphic models. The largest residue in the final difference Fourier map (near the Rh(1) atom) was 0.71 e/Å^3. Scattering factors, corrected for anomalous dispersion, were taken from the internal library of SHELX97. Relevant bond distances and angles are supplied in the caption of Figure 1. The Supporting Information (CIF file) comprises the full list of fractional atomic coordinates, bond distances and angles, and anisotropic displacement parameters.

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Supporting Information Available: ^{1}H NMR spectra (hydridic region) for compounds **1**−**3** and a complete crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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