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Rhodium carbonyl complexes of bulky, anionic nitrogen-based ligands: A comparison of donating ability[☆]

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ABSTRACT

Phosphinimine-imine $((C_6H_3\textit{i}\text{-}Pr_2)NC(Me)CH_2PPh_2(NC_6H_3\textit{i}\text{-}Pr_2))Rh(CO)_2$ – (**1**) and β-diketiminate $CH(C(Me)(N\textit{i}\text{-}Pr_2C_6H_3))_2Rh(CO)_2$ – (**2**) rhodium dicarbonyl complexes were prepared as to elucidate any difference among these anionic, nitrogen-based ligands regarding donating ability to the rhodium center. Utilizing infrared spectroscopy and single crystal structural comparisons, differences in electron density donation by the ligands to the rhodium center were not observed. The carbonyl stretching frequencies of the aforementioned rhodium complexes were $\nu_{CO} = 2055, 1987$ and 2055, 1988 for the phosphinimine-imine (**1**) and β-diketiminate (**2**) respectively.

1. Introduction

The development of sterically bulky nitrogen-based ligand systems for use in late transition metal compounds was accelerated by the discovery of highly active nickel-based olefin polymerization catalysts using the sterically bulky α-diimine ligand [1]. These ligand systems generally form five- or six-membered metal chelates, thus a number of structural perturbations of these systems have been developed, either by altering the composition of the ligand backbone or by altering the electronic or steric properties of the peripheral substituents. The phosphinimine-imine ligand [2–5] is shown to exhibit properties similar to both the NacNac (β-diketiminate) [6–10] style of ligand and bisphosphinimine ligand systems [11–15] which have recently used in support of catalytically active metal centers for lactide polymerization [16]. The extremely sterically bulky imidoylamidine ligand readily forms late metal dihalide complexes, however the reactivity of these complexes is greatly diminished compared to their less bulky counterparts [17]. The synthesis of two, rhodium(I) complexes is described, including structural characterization and infrared analysis as to determine potential differences in donating ability among sterically similar phosphinimine-imine and β-diketiminate ligands. During the preparation of this manuscript, the β-diketiminate rhodium dicarbonyl complex $CH(C(Me)(N\textit{i}\text{-}Pr_2C_6H_3))_2Rh(CO)_2$, **2**, was published [18].

2. Experimental

2.1. General data

All preparations were done under an atmosphere of dry, O_2-free N_2 employing both Schlenk line techniques and an mBraun glove box. Toluene, pentane, and THF were purified employing a Grubbs' type solvent purification system. Deuterated solvents were dried over Na/benzophenone (C_6D_6, toluene-d_8). ^1H, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker Avance-300. Trace amounts of protonated solvent were used as internal references for ^1H NMR spectra (C_6D_5H δ 7.16 ppm). The deuterated solvent was used as an internal reference for $^{13}C\{^1H\}$ NMR spectra. The chemical shifts for both ^1H and $^{13}C\{^1H\}$ are reported relative to tetramethylsilane. $^{31}P\{^1H\}$ was referenced to external 85% H_3PO_4. Coupling constants are reported as absolute values. Combustion analyses were done in house employing a PerkinElmer CHN Analyzer. IR spectra were recorded using a Bruker VECTOR 22 infrared Fourier transform spectrometer. *n*-BuLi (1.6 M in hexanes) was purchased from the Aldrich Chemical Company and used as received. Hyflo Super Cel® (celite) was purchased from Aldrich Chemical Company and dried for 24 h in a vacuum oven prior to use. Molecular sieves (4 Å) were purchased from Aldrich Chemical Co. and dried at 140 °C

[☆] Electronic Supplementary Information (ESI) available: Crystallographic data.

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under vacuum using a rotary vacuum pump. $(Rh(CO)_2Cl)_2$ was purchased from Strem Chemicals Inc. while NacNacH [19] and $(C_6H_3i\text{-}Pr_2)NC(Me)CH_2PPh_2(NC_6H_3i\text{-}Pr_2)$ [3] were prepared according to literature methods.

2.2. Synthesis of phosphinimine-imine and NacNacRh complexes

2.2.1. Synthesis of $((C_6H_3i\text{-}Pr_2)NC(Me)CH_2PPh_2(NC_6H_3i\text{-}Pr_2))Rh(CO)_2$ – **1**

To a solution of 102 mg (0.177 mmol) of $(C_6H_3i\text{-}Pr_2)NC(Me)CH_2PPh_2(NC_6H_3i\text{-}Pr_2)$ in 5 mL THF was added one equivalent of *n*-BuLi (0.111 mL of a 1.6 M solution in hexanes) and the mixture was allowed to stir for 2 h. Then 34 mg (0.18 mmol) of $(Rh(CO)_2Cl)_2$ added to the solution. After stirring overnight, the solvent was removed *in vacuo*. The solids were washed with 10 mL of toluene and the yellow solution filtered through celite. Upon cooling to −35 °C overnight, 85 mg of bright yellow blocks were isolated by decantation and washing with pentane. Yield: 65%. ^{1}H NMR (C_6D_6) δ: 7.80–7.86 (m, 4H, *o*-PPh_2), 7.01–7.10 (m, 12H, *m*, *p*-PPh_2, *m*, *p*-Ar), 4.09 (sept, 2H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 3.27 (d, 1H, $^{2}J_{P-H} = 27$ Hz, PC*H*), 3.27 (sept, 2H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.60 (d, 6H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.56 (s, 3H, Me), 1.25 (d, 6H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.14 (d, 6H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.06 (d, 6H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (C_6D_6) δ: 185.9 (d, $^{1}J_{Rh-C} = 67.5$ Hz, $Rh(CO)_2$), 167.8, 157.3, 146.2, 142.7, 137.0, 133.9, 133.8, 131.5,131.1, 127.7–128.3 (m, obscured by C_6D_6), 125.9, 124.6, 123.9, 70.0 (d, $^{1}J_{P-C} = 121$ Hz, PCH), 29.2, 28.2, 26.0, 24.6, 23.7. $^{31}P\{^{1}H\}$ NMR (C_6D_6) δ: 18.1. IR (KBr pellet): 2055 (symmetric ν_{CO}), 1987 (asymmetric ν_{CO}) cm^{-1}. Anal. Calc. for $C_{41}H_{48}N_2PRhO_2$: C, 67.02; H, 6.59; N, 3.81. Found: C, 67.39; H, 6.88; N, 3.82.

2.2.2. Synthesis of $CH(C(Me)(Ni\text{-}Pr_2C_6H_3))_2Rh(CO)_2$ – **2**

To a solution of 108 mg (0.257 mmol) of NacNacH in 5 mL THF was added one equivalent of *n*-BuLi (0.161 mL of a 1.6 M solution) and the mixture was allowed to stir for 2 h. Then 50 mg (0.257 mmol) of $(Rh(CO)_2Cl)_2$ in 2 mL THF was added dropwise to the solution. After stirring overnight the solvent was removed *in vacuo*. The solids were washed with 8 mL of toluene and the yellow solution filtered through celite. Upon cooling to −35 °C overnight, 74 mg of bright yellow blocks were isolated by decantation and washing with pentane. Yield: 50%. ^{1}H NMR (toluene-d_8) δ: 6.97–7.12 (m, 6H, *m*, *p*-Ar), 5.09 (s, 1H, C*H*), 3.39 (sept, 4H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.68 (s, CH_3), 1.46 (d, 12H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$), 1.15 (d, 12H, $^{3}J_{H-H} = 7$ Hz, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (toluene-d_8) δ: 184.9 (d, $^{1}J_{Rh-C} = 68$ Hz, $Rh(CO)_2$), 160.4, 155.5, 140.6, 126.7, 123.8, 97.6 (CH), 28.2, 24.1, 23.9, 22.8. IR (KBr pellet): 2055 (symmetric ν_{CO}), 1988 (asymmetric ν_{CO}) cm^{-1}. Anal. Calc. for $C_{31}H_{41}N_2RhO_2$: C, 64.58; H, 7.17; N, 4.86. Found: C, 64.65; H, 7.36; N, 4.79.

2.3. X-ray data collection, reduction, solution and refinement

Single crystals of **1** were mounted in a thin-walled capillary (**1**) and data collected at room temperature. Single crystals of **2** were placed in oil and mounted in a nylon loop and cooled to 123 K using an Oxford Cryostream cooling system. The data were collected using the Bruker APEX2 software package [20,21] on a Siemens diffractometer equipped with an APEXII CCD detector, a graphite monochromator and Mo Kα radiation (λ = 0.71073 Å). A hemisphere of data was collected in 1664 frames with 10 s exposure times. Data processing and absorption corrections were applied using APEX2 software package. The structure was solved (direct methods) and all non-H atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions using an appropriate riding model and coupled isotropic temperature factors. ORTEP-III [22] renderings with selected bond lengths and angles are provided in Figs. 2 and 3. Selected crystallographic data are included in Table 1.

Table 1
Selected crystallographic data for compounds **1** and **2**.

Compound	1	2
Formula	$C_{41}H_{48}N_2O_2PRh$	$C_{31}H_{41}N_2RhO_2$
Formula weight	734.69	576.57
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	C2/c
a (Å)	11.934(3)	35.240(9)
b (Å)	14.590(3)	9.354(2)
c (Å)	21.632(5)	20.881(5)
β (°)	90.972(6)	120.631(3)
V ($Å^3$)	3766 (2)	5922(3)
Z	4	8
Temperature (K)	297	123
Density (calc, g/cm^3)	1.296	1.293
Abs coeff. (mm^{-1})	0.532	0.605
Reflections collected	18,586	18,873
Independent reflections	5463	5213
Variables	432	324
R_1	0.0409	0.0297
R_w	0.08559	0.0695
GOF	0.993	0.979
Largest diff. peak and hole (e $Å^3$)	0.465 and −0.203	0.695 and −1.211

Data collected with Mo Kα radiation (λ = 0.71069 Å).
$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma[\omega(F_o^2 - F_c^2)^2]/\Sigma[\omega(F_o^2)^2]]^{0.5}$.

3. Results and discussion

Reaction of $(C_6H_3i\text{-}Pr_2)NC(Me)CH_2PPh_2(NC_6H_3i\text{-}Pr_2)Li$ (prepared *in situ*) with an equimolar amount of $(Rh(CO)_2Cl)_2$ gave bright yellow, analytically pure crystals of **1** upon workup (Fig. 1). In a similar reaction, NacNacLi (prepared *in situ* from *n*-BuLi and NacNacH) was reacted with $(Rh(CO)_2Cl)_2$ to give dark yellow crystals of **2** (Fig. 1). ^{1}H and $^{13}C\{^{1}H\}$ NMR spectral data were consistent with the formation of the rhodium carbonyl compounds, with the Rh-bound carbonyl peaks appearing in the ^{13}C NMR spectrum as a doublet at 185.9 ppm ($^{1}J_{Rh-C} = 67.5$ Hz) for **1** and 184.9 ($^{1}J_{Rh-C} = 68$ Hz) for **2**, in agreement with other examples in the literature [23]. The ^{1}H NMR spectrum of **2** reveals the highly symmetric nature of this molecule, featuring one septet for the methine and one doublet for the methyl protons of the four *i*-Pr groups as well as one signal for the imine–C–CH_3 groups. This is in contrast to **1** in which the dissymmetric ligand features two sets of *i*-Pr signals from the imine-Ar and phosphinimine-Ar groups. In addition, the IR spectrum of **1** showed peaks at 2055 and 1987 cm^{-1}, consistent with symmetric and asymmetric metal dicarbonyl stretches, respectively, while the spectrum of **2** featured peaks at 2055 and 1988 cm^{-1}. These results show that there is no

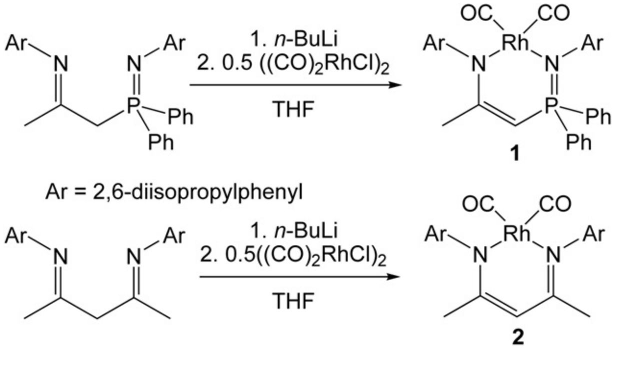
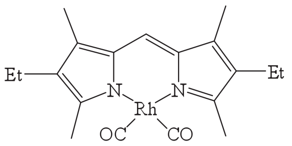


Fig. 1. Synthesis of rhodium dicarbonyl complexes.

Table 2
Carbonyl stretching frequencies for selected rhodium compounds.

Compound	ν_{CO} (cm^{-1})	Reference
$[Rh(TMEDA)(CO)_2][ClO_4]$	2080–2010[a]	[26]
$[CH_2((Ph_2)PN(4\text{-}CH_3C_6H_4))_2Rh(CO)_2][Cl]$	2077, 2012	[11]
	2080, 2010	[27]
$[CH_2(C(Me)NH)_2Rh(CO)_2][BF_4]$	2090, 2040	[24]
$CH(C(Me)(N\textit{i}\text{-}Pr_2C_6H_3))(P(Ph_2)(N\textit{i}\text{-}Pr_2C_6H_3)Rh(CO)_2$ – **1**	2055, 1987	This work
$CH(C(Me)(N\textit{i}\text{-}Pr_2C_6H_3))_2Rh(CO)_2$ – **2**	2055, 1988	This work

[a] A range is reported for both peaks.

difference between the two ligand systems in their donating ability to the rhodium metal center. This finding is intriguing considering that phosphinimine-based systems are thought to be relatively good donors due to the $R_3P^+{-}N^-R'$ resonance structure that can be formulated. However, these CO stretches are significantly lower in energy compared to other diamine and bisphosphinimine ligands in the literature (Table 2), making these ligands featured in **1** and **2** to be excellent choices for producing electron-rich metal centers.

A single crystal X-ray diffraction study of **1** revealed a square planar Rh center, with two carbonyl ligands located *trans* to the imine and phosphinimine nitrogen atoms that fill the coordination sphere (Fig. 2). The phosphorus atom is highly distorted from the other atoms of the six-membered chelate, deviating 0.6944 Å from the mean plane defined by N(1)–Rh(1)–N(2)–C(4)–C(3). The Rh–N bond lengths are 2.099(3) and 2.109(3) Å, slightly longer than those in $[HC(CNH)_2Rh(CO)_2][BF_4]$ (2.036(3) and 2.045(4) Å) [24] and in $(HC(1,2\text{-}(CN)_2(C_6H_4))Rh(CO)_2)_2$ (average 2.071(4) Å) [25]. The Rh–C bond lengths are 1.837(5) and 1.844(5) Å, shorter than those reported for $[HC(CNH)_2Rh(CO)_2][BF_4]$ (1.864(5) and 1.881(6) Å) and $(HC((1,2\text{-}(CN)_2(C_6H_4))Rh(CO)_2)_2$ (average 1.864(6) Å), indicating a stronger back-bonding interaction between the metal and carbonyl ligands in **1**. In addition, the C–O bond lengths are longer in **1** (1.144(5) and 1.145(5) Å) than in $[HC(CNH)_2Rh(CO)_2][BF_4]$ (1.119(6) and 1.104(7) Å). These longer bond lengths are reflected in the lower frequency of C–O stretches in **1** (Table 2) and agree with the stronger back bonding in **1**. Crystallographic characterization of **2** also reveals a square planar arrangement around the Rh center (Fig. 3). In contrast to **1**, the Rh–NacNac six-membered chelate is essentially planar. The Rh–N bond distances were shorter than in the phosphinimine-imine complex at 2.050(2) and 2.052(2) Å. Conversely the Rh–C bond lengths were found to be longer, being 1.864(2) and 1.867(2) Å respectively. These differences did not manifest themselves in longer C–O bonds in **2**. These were found to be 1.142(3) and 1.142(3) Å, within the uncertainty of those found in **1**. The similar C–O bond distances in complexes **1**–**2** are supported by the infrared data for these compounds.

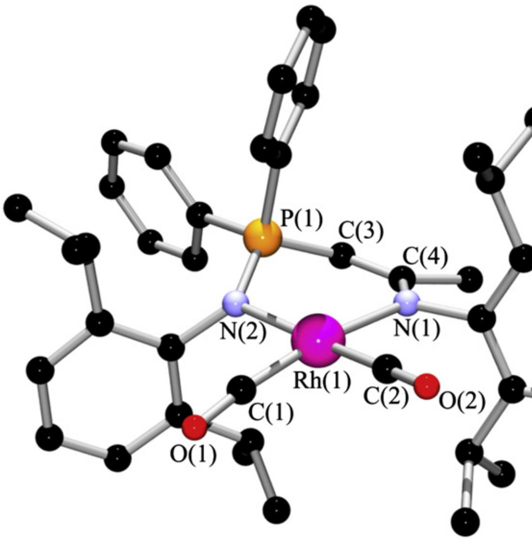


Fig. 2. ORTEP-III rendering of **1** (50% probability). Hydrogen atoms are omitted for clarity. Distances (Å) angles (°): Rh(1)–C(1) 1.837(5), Rh(1)–C(2) 1.844(5), Rh(1)–N(2) 2.099(3), Rh(1)–N(1) 2.109(3), P(1)–N(2) 1.610(3), P(1)–C(3) 1.726(4), O(1)–C(1) 1.143(5), O(2)–C(2) 1.145(5), C(1)–Rh(1)–C(2) 87.01(19), C(1)–Rh(1)–N(2) 88.16(16), C(2)–Rh(1)–N(2) 171.81(18), C(1)–Rh(1)–N(1) 171.60(19), C(2)–Rh(1)–N(1) 91.23(16), N(2)–Rh(1)–N(1) 94.49(12), N(2)–P(1)–C(3) 113.0(2), C(4)–N(1)–Rh(1) 128.5(3), P(1)–N(2)–Rh(1) 113.33(16), O(1)–C(1)–Rh(1) 174.1(5), O(2)–C(2)–Rh(1) 173.7(5), C(4)–C(3)–P(1) 122.4(3), C(3)–C(4)–N(1) 124.5(4).

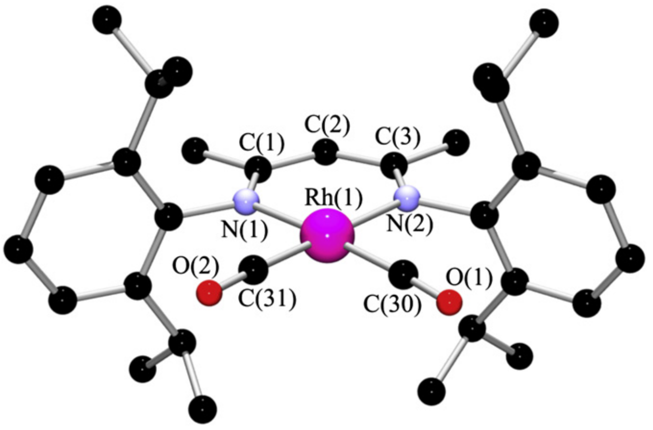


Fig. 3. ORTEP-III rendering of **2** (50% probability). Hydrogen atoms are omitted for clarity. Rh(1)–C(31) 1.864(2), Rh(1)–C(30) 1.867(2), Rh(1)–N(1) 2.050(2), Rh(1)–N(2) 2.052(2), N(2)–C(3) 1.329(3), N(1)–C(1) 1.332(3), C(2)–C(1) 1.395(3), C(2)–C(3) 1.400(3), C(30)–O(1) 1.142(3), C(31)–O(2) 1.142(3), C(31)–Rh(1)–C(30) 85.78(10), C(31)–Rh(1)–N(1) 92.51(9), C(30)–Rh(1)–N(1) 176.51(9), C(31)–Rh(1)–N(2) 177.19(9), C(30)–Rh(1)–N(2) 92.05(9), N(1)–Rh(1)–N(2) 89.75(8), C(3)–N(2)–Rh(1) 126.89(16), C(1)–N(1)–Rh(1) 126.73(16), C(1)–C(2)–C(3) 128.0(2), N(2)–C(3)–C(2) 124.2(2), N(1)–C(1)–C(2) 124.4(2), O(1)–C(30)–Rh(1) 176.5(2), O(2)–C(31)–Rh(1) 176.0(2).

In conclusion, the traditional back-bonding model for the explanation of relative carbonyl stretching frequencies in metal complexes may suggest differences in the donating ability from otherwise analogous phosphinimine-imine and β-diketiminate anionic ligand systems however, the findings herein do not make such a distinction indicating that both ligands have similar electron donating capabilities.

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Appendix A. Supplementary material

CCDC 814888 for **1** and 814889 for **2** contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

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