

Supporting Information:

A 4-Coordinate Ru(II) Imido: Unusual Geometry, Synthesis, and Reactivity

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General: All reactions and manipulations were carried out in an MBraun glovebox under a nitrogen atmosphere and/or using standard Schlenk techniques. Solvents were purchased from Aldrich Chemical Co. and purified either by distilling from sodium-benzophenone ketyl or by passing through alumina columns to remove water after sparging with dinitrogen to remove oxygen. $\text{Cl}_2\text{Ru}(\text{PPh}_3)_3$ was prepared using the literature procedure from $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ purchased from Pressure Chemical Company.¹ PPh_3 and PMe_3 were purchased from Aldrich Chemical Company and used as received. H_2NAr (where Ar = 2,6-diisopropylphenyl) was purchased from Aldrich Chemical Co. and was distilled from KOH under dry nitrogen then stored under inert atmosphere. LiNHAr was prepared by treating H_2NAr in pentane with 1 equiv. of 1.6 M LiBu^n in hexanes, and the precipitated white product was collected by filtration then dried in vacuo. Deuterated benzene and chloroform were purchased from Cambridge Isotopes Laboratories, Inc. and distilled from sodium-benzophenone ketyl (benzene) or calcium hydride (chloroform). NMR spectra were taken on Varian UNITY plus 500 spectrometer equipped with a 5 mm Pulsed-Field-Gradient (PFG) switchable broadband probe, operating at 500 MHz (^1H), 202 MHz (^{31}P) or 126 MHz (^{13}C). NMR chemical shifts are reported in ppm and referenced to the solvent peaks for ^1H ($\text{C}_6\text{D}_5\text{H}$, δ 7.16 ppm; CDCl_3 , δ 7.26 ppm) and ^{13}C (natural abundance ^{13}C in C_6D_6 , δ 128.06 ppm) NMR. ^{31}P NMR chemical shifts are referenced to an external 85% H_3PO_4 standard as 0 ppm.

Synthesis of cis-Ru(PMe₃)₄Cl₂: In a glove box, *trans*- $\text{RuCl}_2(\text{PPh}_3)_3$ (2 g, 2.1 mmol) was dissolved in toluene (20 mL) in a pressure tube, and trimethylphosphine (1.52 mL, 14.7 mmol) was added. The pressure tube was sealed, taken out of the glove box, and heated at 100 °C for 20 h. The pressure tube was brought back inside the glove box, and solvent was removed in vacuo. The residue was washed with pentane (3 × 20 mL) and filtered to get a pale yellow solid. If the solid appeared green, it was dissolved in dichloromethane, filtered through Celite, and the yellow

1. Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

filtrate was dried to get pure compound. The pale yellow solid was recrystallized from CH₂Cl₂-pentane (1:1, v/v) at -35 °C. Yield: 915 mg (92%). ¹H NMR (500 MHz, CDCl₃, 25 °C): δ 1.55 (t, *J* = 3.2 Hz, 18H), 1.49 – 1.45 (m, 18H). ³¹P{¹H} NMR (202 MHz, CDCl₃, 25 °C): δ 11.17 (t, *J* = 32.7 Hz), -10.68 (t, *J* = 32.7 Hz). M.P. Obvious decomp did not occur until 392 °C.

Synthesis of Ru(PMe₃)₃(NAr) (1): In an Erlenmeyer flask, *cis*-RuCl₂(PMe₃)₄ (1.61 g, 3.38 mmol) and LiNHAr (Ar = 2,6-diisopropylphenyl) (1.30 g, 7.10 mmol) were mixed under a nitrogen atmosphere, and cold THF (50 mL, *ca.* -70 °C) was added. The reaction was allowed to come to room temperature and stirred for 15 h when the color changed from light yellow to dark orange. The solvent was removed in vacuo. The residue was extracted with pentane several times until the pentane extract was colorless, and the mixture was filtered through Celite. The pentane solution was concentrated (~10 mL) in vacuo and kept in the fridge at -35 °C to get dark red crystals of **1** (1.13 g, 66%). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 7.13 (s, 3H, C₆H₃), 4.47 – 4.37 (sept, *J* = 7.0 Hz, 2H, CH(CH₃)₂), 1.41 (d, *J* = 7.0 Hz, 12H, CH(CH₃)₂), 1.29 (s, 27H, P(CH₃)₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ 157.92 (q, ⁴*J*_{P-C} = 4.4 Hz, C₆H₃), 139.91 (q, ³*J*_{P-C} = 5.8 Hz, C₆H₃), 122.23 (q, ⁶*J*_{P-C} = 1.3 Hz, C₆H₃), 119.52 (q, ⁵*J*_{P-C} = 1.6 Hz, C₆H₃), 26.83 (s, CH(CH₃)₂), 26.32 – 26.06 (m, P(CH₃)₃), 23.54 (s, CH(CH₃)₂). ³¹P{¹H} NMR (202 MHz, C₆D₆, 25 °C): δ 19.6 (s). Anal. Calcd. for C₂₁H₄₄NP₃Ru: C, 49.99; H, 8.79; N, 2.78. Found: C, 50.07; H, 9.12; N, 2.87. M.P. 118-122 °C.

Synthesis of (PMe₃)₃Ru(κ-N:κ-N:μ-NAr)CuI (2): Under a nitrogen atmosphere, a scintillation vial was loaded with **1** (60 mg, 0.12 mmol), CuI (25 mg, 0.132 mmol), and toluene (5 mL). The reaction was stirred at room temperature for 3 h. Then, the reaction mixture was filtered through Celite, concentrated in vacuo to ~1.5 mL, and kept at -35 °C to get dark brown crystals of **2** (72 mg, 80%). ¹H NMR (500 MHz, C₆D₆, 25 °C): δ 7.12 (dd, *J* = 8.4, 6.5 Hz, 1H, C₆H₃), 7.09 – 7.04 (m, 2H, C₆H₃), 3.98 (sept, *J* = 7.0 Hz, 2H, CH(CH₃)₂), 1.45 (d, *J* = 6.8 Hz, 6H, CH(CH₃)₂), 1.29 (d, *J* = 7.1 Hz, 6H, CH(CH₃)₂), 1.17 – 1.13 (m, 27H, P(CH₃)₃). ¹³C{¹H} NMR (126 MHz, C₆D₆, 25 °C): δ 155.12 (d, *J* = 2.2 Hz, C₆H₃), 141.31 (q, *J* = 3.9 Hz, C₆H₃), 123.01 (s, C₆H₃), 122.80 (s, C₆H₃), 26.79 (s, CH(CH₃)₂), 26.53 (s, CH(CH₃)₂), 24.11 – 23.83 (m, P(CH₃)₃), 21.97 (s, CH(CH₃)₂). ³¹P{¹H} NMR (202 MHz, C₆D₆, 25 °C): δ 19.3 (s). Anal. Calcd. for C₂₁H₄₄NCuIP₃Ru: C, 36.29; H, 6.38; N, 2.02. Found: C, 36.54; H, 6.64; N, 2.05. M.P. 132-134 °C.

*³¹P NMR study of the equilibrium between $Ru(PMe_3)_3\{N(H)Ar\}\{N(H)NC_5H_{10}\}$ (**3**), $Ru(PMe_3)_3(NNC_5H_{10})$ (**4**), and **1**:* In an NMR tube, **1** (13 mg, 0.0258 mmol) was dissolved in C_6D_6 (0.5 mL), and 1-aminopiperidine (3 μ L, 0.0278 mmol) was added. $^{31}P\{^1H\}$ NMR was recorded at 25 °C. Longitudinal relaxation times (T_1) for the three ^{31}P NMR signals were determined from an inversion recovery experiment. For a reliable integration of ^{31}P NMR peaks in the equilibrium, the relaxation delay was set to 25 s, more than five times of longest T_1 (4.3 s). Two spectra were recorded before and after adding 10 equiv. of 2,6-diisopropylaniline (49 μ L, 0.260 mmol). The number of scans was kept at 128 for all experiments. Peaks for **1**, **3** and **4** were identified as δ 17.9, 5.9 and 15.2 ppm, respectively. Observed percentage at equilibrium without adding 2,6-diisopropylaniline: **1**, 7.8%; **3**, 19.1%; **4**, 73.1%. Observed percentage at equilibrium with 10 equivalents of 2,6-diisopropylaniline: **1**, 26.5%; **3**, 23.7%; **4**, 49.8%.

*³¹P NMR study of the equilibrium between $Ru(PMe_3)_3\{N(H)Ar\}\{N(H)NMe_2\}$, $Ru(PMe_3)_3(NNMe_2)$, and **1**:* In an NMR tube, **1** (13 mg, 0.026 mmol) was dissolved in C_6D_6 (0.5 mL), and *N,N*-dimethylhydrazine (2 μ L, 0.026 mmol) was added. $^{31}P\{^1H\}$ NMR was recorded at 25 °C. The relaxation delay was set to 25 s assuming longitudinal relaxation times (T_1) to be similar to those of **3** and **4**. The number of scans was 128. Peaks for $Ru(PMe_3)_3\{N(H)Ar\}\{N(H)NMe_2\}$, $Ru(PMe_3)_3(NNMe_2)$, and **1** were assigned as δ 19.6, 7.0 and 15.0 ppm, respectively. The peak for **1** was obviously known. The chemical shifts for the other two species in solution were assumed to be the analogues of the compounds with 1-aminopiperidine as the chemical shifts are quite similar. The observed percentages at equilibrium were: **1**, 14.5 %; $Ru(PMe_3)_3\{N(H)Ar\}\{N(H)NMe_2\}$, 3.1%; $Ru(PMe_3)_3(NNMe_2)$, 82.4%. Attempts to isolate either the hydrazido(1-) or hydrazido(2-) from these mixtures resulted in re-isolation of starting material **1**, presumably the most crystalline compound in the equilibrium mixture.

*Isolation of **3** for X-ray diffraction and data for **4** in solution:* Under a nitrogen atmosphere, a scintillation vial was loaded with **1** (60 mg, 0.12 mmol) in pentane (5 mL) and 1-aminopiperidine (14 μ L, 0.132 mmol) was added. The reaction was stirred at room temperature for 1 h, concentrated in vacuo to ~2 mL, and kept at -35 °C to get red-brown crystals of **3** (61 mg, 78%). Anal. Calcd. for $C_{26}H_{56}N_3P_3Ru$: C, 51.64; H, 9.33; N, 6.95. Found: C, 51.07; H, 10.07; N, 6.37. M. P. 138-142 °C. $^{31}P\{^1H\}$ NMR (202 MHz, C_6D_6 , 25 °C): δ 5.7 (s). *Data for **4***

in solution: ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 7.05 (d, $J = 7.7$ Hz, 2H), 6.89 (t, $J = 7.6$ Hz, 1H), 3.23 (s, 2H), 2.93 – 2.86 (m, 4H), 2.66 (sept, $J = 6.8$ Hz, 2H), 1.57 (dt, $J = 11.5, 5.9$ Hz, 4H), 1.42 – 1.39 (m, 27H), 1.15 (d, $J = 6.8$ Hz, 12H), 0.87 (t, $J = 7.2$ Hz, 2H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6 , 25 °C): δ 15.0 (s). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 25 °C): δ 140.79 (s), 132.33 (s), 123.13 (s), 118.91 (s), 69.83 (q, $J = 4.6$ Hz), 56.70 (q, $J = 5.8$ Hz), 28.84 – 28.61 (m), 28.19 (s), 22.63 (s).

*Synthesis of $\text{Ru}(\text{PMe}_3)_3\{\kappa\text{-N}(\text{Ar});\kappa\text{-O:N}(\text{Ar})\text{C}(\text{O})\text{NPh}\}$ (**5**)*: Under a nitrogen atmosphere, a scintillation vial was loaded with **1** (60 mg, 0.12 mmol) in toluene (1.5 mL) and phenylisocyanate (14 μL , 0.132 mmol) was added. The reaction was stirred at room temperature for 3 h and then kept at -35 °C for 3 d to get red crystals of **5** (72 mg, 80%). ^1H NMR (500 MHz, C_6D_6 , 25 °C): δ 7.81 (d, $J = 7.6$ Hz, 2H), 7.35 – 7.31 (m, 2H), 7.27 – 7.19 (m, 3H), 6.90 (t, $J = 7.2$ Hz, 1H), 3.73 (sept, $J = 6.9$ Hz, 2H), 1.66 (d, $J = 6.8$ Hz, 6H), 1.41 (d, $J = 7.0$ Hz, 6H), 0.94 (dd, $J = 5.9, 2.9$ Hz, 27H). $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, C_6D_6 , 25 °C): δ 27.0 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 25 °C): δ 173.32 (s), 152.48 (s), 147.00 (s), 143.98 (dd, $J = 2.9, 1.5$ Hz), 125.55 (s), 124.10 (s), 122.60 (s), 122.19 (s), 118.95 (s), 28.18 (s), 26.21 (s), 23.10 (s), 20.28 (d, $J = 28.9$ Hz). Anal. Calcd. for $\text{C}_{28}\text{H}_{49}\text{N}_2\text{OP}_3\text{Ru}$: C, 53.92; H, 7.92; N, 4.49. Found: C, 53.52; H, 7.61; N, 4.42. M.p. 136 °C (dec).

Computational Methods

Computational work was performed on a model complex, $\text{Ru}(\text{NH})(\text{PH}_3)_3$. The geometry was optimized at the quadratic configuration interaction with single and double excitations and non-iterative triples correction (QCISD(T)) level of theory,² yielding bond angles and lengths in good agreement with those observed in the crystal structure of the fully substituted complex. The cc-pVTZ-PP basis³ and effective core potentials were applied to ruthenium, while cc-pVDZ⁴ was applied to the remainder of the molecule. Constrained optimizations, with bond angles and dihedrals constrained to produce a perfectly tetrahedral arrangement of ligands around the

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3. Peterson, K. A.; Figgen, D.; Dolg, M.; Stoll, H. *Journal of Chemical Physics* **2007**, *126*.

4. (a) Dunning, T. H. *Journal of Chemical Physics* **1989**, *90*, 1007. (b) Woon, D. E.; Dunning, T. H. *Journal of Chemical Physics* **1993**, *98*, 1358.

ruthenium atom, were performed as well. Complete active space self-consistent field⁵ calculations, using an active space of ten electrons in ten orbitals (CAS(10/10)) and the same basis set as above, were performed to investigate the presence of radical electrons. The number of unpaired electrons on each atom was estimated by performing Mulliken analysis of the density of effectively unpaired electrons (EUE) as defined by Staroverov and Davidson.⁶ The orbitals presented in the main text are natural orbitals of the QCISD(T) wavefunction.

Diradical character was found across the Ru–N bond during the calculations on the HN= Ru(PH₃)₃ model. The amount of unpaired spin was more than 0.3 unpaired electrons on each site with, as might be expected, the Ru atom having somewhat higher density of effectively unpaired electrons. A plot of the effectively unpaired electrons is shown below in Figure 1.

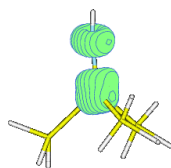


FIGURE 1. The density of effectively unpaired electrons around the model RuNH(PH₃)₃ system.

All calculations were performed with the MolPro suite of ab initio software.⁷

Optimized Molecular Structures

Structures are in .xyz format.

QCISD(T) Optimized Structure

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QCISD(T)/CC-PVDZ, RU=CC-PVTZ-PP Energy: -1177.296995561457  
CAS(10/10)/CC-PVDZ, RU=CC-PVTZ-PP Energy: -1176.34948761
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6. Staroverov, V. N.; Davidson, E. R. *Chemical Physics Letters* **2000**, *330*, 161.

7. MOLPRO is a package of ab initio programs written by H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, M. Schutz, P. Celani, T. Korona, R. Lindh, A. Mitrushenkov, G. Rauhut, K. R. Shamasundar, T. B. Adler, R. D. Amos, A. Bernhardsson, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, E. Goll, C. Hampel, A. Hesselmann, G. Hetzer, T. Hrenar, G. Jansen, C. Koppl, Y. Liu, A. W. Lloyd, R. A. Mata, A. J. May, S. J. McNicholas, W. Meyer, M. E. Mura, A. Nicklass, D. P. O'Neill, P. Palmieri, K. Pfluger, R. Pitzer, M. Reiher, T. Shiozaki, H. Stol, A. J. Stone, R. Tarroni, T. Thorsteinsson, M. Wang and A. Wolf, (2010).

Total number of EUE (CAS(10/10)): 1.0736758
Number of EUE on nitrogen (CAS(10/10)): 0.35026

15
QCISD(T)/CC-PVDZ,RU=CC-PVTZ-PP optimized structure

Ru	-0.2212389927	0.4961238711	0.0000063742
N	-0.7519910078	2.1815154287	-0.0000089588
H	-0.7808899691	3.2159363100	-0.0000371446
P	-0.5122078632	-1.0881154344	-1.6320894792
H	-1.0554033807	-2.3947270597	-1.3906811769
H	-1.3863022781	-0.7470864932	-2.7062014527
H	0.5862333445	-1.5266520844	-2.4423080932
P	-0.5122015329	-1.0881304859	1.6320943873
H	-1.0554000002	-2.3947395057	1.3906774831
H	0.5862379182	-1.5266661094	2.4423165513
H	-1.3862891943	-0.7471063542	2.7062133501
P	2.0188008027	0.2669858358	0.0000056280
H	2.7020158680	-0.3988586244	-1.0701917574
H	2.8218261010	1.4461665540	0.0000084061
H	2.7020201845	-0.3988658482	1.0701958826

Tetrahedrally Constrained QCISD(T) Optimized Structure

QCISD(T)/CC-PVDZ,RU=CC-PVTZ-PP Energy: -1177.268944565017

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QCISD(T)/CC-PVDZ,RU=CC-PVTZ-PP optimized structure with
tetrahedral constraints

N	0.0000000000	0.0000000000	0.0000000000
Ru	0.0000000000	0.0000000000	1.7670140462
P	0.0000000000	2.1370525217	2.5279842195
P	1.8988360215	-1.0992004754	2.5393288993
P	-1.8989504320	-1.0992667055	2.5393754335
H	0.0006363175	0.2492964245	-1.0131444925
H	2.0667275548	-2.1211362039	3.5307212789
H	2.4269971492	-1.8566920502	1.4554778934
H	3.1003446400	-0.3946395348	2.8596655239
H	-2.0634295051	-2.1291924392	3.5229793082
H	-3.0980340539	-0.3958729692	2.8714307874
H	-2.4336235520	-1.8466748281	1.4517473718
H	1.0641239414	2.7212152276	3.2864395433
H	0.0000000000	3.1175021633	1.4885089310
H	-1.0642433672	2.7210750611	3.2863944772

