Supporting Information for

Synthesis and Reactivity of Iridium(III) Dihydrido Aminocarbenes

Matthew T. Whited and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratories of Chemical Synthesis, Division of Chemistry and Chemical Engineering
California Institute of Technology, Pasadena, CA 91125
Experimental Section

All manipulations were carried out using standard Schlenk or glove-box techniques under a dinitrogen atmosphere. Unless otherwise noted, solvents were deoxygenated and dried by thorough sparging with Ar gas followed by passage through an activated alumina column.¹ Hexamethyldisiloxane and t-buty methyl ether were distilled from CaH₂ and degassed prior to use. (PNP)IrH₂² and (PNP)Ir=C(H)O’Bu (I)³ were prepared according to literature procedure. Other reagents were purchased from commercial vendors and used without further purification. Elemental analyses were carried out at Desert Analytics, Tucson, Arizona. NMR spectra were recorded at ambient temperature on Varian Mercury 300 MHz and 500 MHz spectrometers. ¹H and ¹³C NMR chemical shifts were referenced to residual solvent. ³¹P NMR chemical shifts are reported relative to an external standard of 85% H₃PO₄. Infrared spectra were recorded using a Perkin Elmer Spectrum BXII spectrometer. X-ray diffraction studies were carried out in the Beckman Institute Crystallographic Facility on a Bruker KAPPA APEX II diffractometer.

X-ray Crystallography Procedures. X-ray quality crystals were grown as indicated in the experimental procedures for each complex. The crystals were mounted on a glass fiber with Paratone-N oil. Structures were determined using direct methods with standard Fourier techniques using the Bruker AXS software package. In some cases, Patterson maps were used in place of the direct methods procedure.

Preparation of Aminocarbene (2). To a solution of (PNP)IrH₂ (139.7 mg, 0.2243 mmol) in N,N,N’,N’-tetramethylethylenediamine (TMEDA, 10 mL) was added a solution of norbornene

(24.3, mg, 0.258 mmol) in TMEDA (3 mL), causing a gradual lightening of the solution from red to yellow. The mixture was stirred at ambient temperature for 16 h and volatiles were removed in vacuo to afford an orange film (4:1 mixture of $2_{\text{anti}} / 2_{\text{syn}}$ by $^{31}$P NMR). The residues were dissolved as much as possible in pentane (ca. 3.5 mL), filtered, and large orange blocks of $2_{\text{anti}}$ were recovered by slow evaporation of pentane at ambient temperature (58.1 mg, 35%). Characterization data for $2_{\text{anti}}$: $^1$H NMR (C$_6$D$_6$): $\delta$ 12.80 (s, 1H, Ir=C(H)N), 7.88 (dt, $J_1 = 8.7$ Hz, $J_2 = 2.1$ Hz, 2H, Ar–H), 7.03 (m, 2H, Ar–H), 6.78 (dd, $J_1 = 8.7$ Hz, $J_2 = 1.8$ Hz, 2H, Ar–H), 3.12 (s, 3H, –NC$_3$H$_3$), 2.76 (t, $^3$J$_{HH} = 6.3$ Hz, 2H, –NCH$_2$), 2.30 (s, 6H, Ar–CH$_3$), 2.20 (m, 4H, –CH(CH$_3$)$_2$), 1.90 (t, $^3$J$_{HH} = 6.3$ Hz, 2H, –NCH$_2$), 1.80 (s, 6H, –N(CH$_3$)$_3$), 1.30 – 1.09 (m, 24H, –CH(C$_3$H$_2$)$_2$), –8.90 (br s, 2H, Ir–H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$): $\delta$ 209.1 (Ir=C(H)N), 162.6 (t, $J = 9$ Hz), 131.0, 125.8, 125.6, 122.7, 115.8, 61.3, 57.4, 45.4, 42.8, 26.9 (t, $J = 16$ Hz), 21.1, 19.1, 18.9. $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 49.1 (s). Anal. Calcd. for C$_{32}$H$_{56}$IrN$_3$P$_2$: C, 52.15; H, 7.66; N, 5.70. Found: C, 52.43; H, 7.43; N, 5.60.

Although $2_{\text{syn}}$ could not be isolated, it was observed by NMR spectroscopy upon equilibration of $2_{\text{anti}}$ in solution: $^1$H NMR (C$_6$D$_6$): $\delta$ 12.76 (s, 1H, Ir=C(H)N). $^{31}$P{$^1$H} NMR (C$_6$D$_6$): $\delta$ 47.2 (s).

**Preparation of Aminocarbene (3).** (PNP)IrH$_2$ (67.2 mg, 0.108 mmol) was dissolved in N-methylmorpholine (7 mL) and norbornene (14.6 mg, 0.155 mmol) was added as a solution in N-methylmorpholine (3 mL), causing a change in color from red to red-brown. The reaction was allowed to proceed 12 h, volatiles were removed in vacuo, and the residues were extracted into pentane, filtered, and dried to a reddish film. Analytically pure 3 was obtained as red-orange crystals by slow evaporation of pentane from a concentrated solution (10.0 mg, 13%). $^1$H NMR (C$_6$D$_6$): 12.70 (s, 1H, Ir=C(H)N), 7.85 (dt, $J_1 = 8.4$ Hz, $J_2 = 2.4$ Hz, 2H, Ar–H), 6.99 (m, 2H, Ar–
$H$, 6.77 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.8$ Hz, 2H, Ar–$H$), 4.08 (m, 2H, morpholine $CH_2$), 3.30 (t, $^3J_{HH} = 4.8$ Hz, morpholine $CH_2$), 3.02 (t, $^3J_{HH} = 4.8$ Hz, morpholine $CH_2$), 2.57 (t, $^3J_{HH} = 4.8$ Hz, morpholine $CH_2$), 2.28 (s, 6H, Ar–$CH_3$), 2.15 (m, 4H, –$CH(CH_3)_2$), 1.18 (dvt, 12H, –$CH(C(CH_3)_2)_2$), 1.09 (dvt, 12H, –$CH(CH_3)_2$), –8.92 (br s, 2H, Ir–$H$).

$^{13}C$ ($^1H$) NMR (C$_6$D$_6$): δ 207.9 (Ir=C(H)N), 162.5 (t, $J = 9.3$ Hz), 131.2, 131.0, 125.3, 123.0, 115.8, 66.6, 66.2, 61.5, 34.8, 26.7 (t, $J = 16$ Hz), 23.1, 21.0, 19.0, 18.9, 14.6, 2.4. $^{31}P$ ($^1H$) NMR (C$_6$D$_6$): δ 49.5 (s). Anal. Calcd. for C$_{31}$H$_{51}$IrN$_2$OP$_2$: C, 51.58; H, 7.12; N, 3.88. Found: C, 52.30; H, 7.12; N, 3.89.

**Preparation of Complex (4).** Aminocarbene 2 (28.1 mg, 0.0381 mmol) was dissolved in benzene (5 mL) and an excess of trimethylphosphine (500 µ, 1.0 M in toluene) was added. The solution was heated at 70 °C for 12 h in a sealed vial, causing lightening to a fluorescent yellow hue. Volatiles were removed in vacuo, leaving a pale yellow film. Analytically pure crystals of 4 suitable for X-ray diffraction were obtained by slow evaporation of pentane from a concentrated solution (28.0 mg, 90%). $^1H$ NMR (C$_6$D$_6$): δ 7.75 (d, $J = 8.7$ Hz, 2H, Ar–$H$), 7.12 (m, 2H, Ar–$H$), 6.78 (d, $J = 8.7$ Hz, 2H, Ar–$H$), 3.21 (m, 2H, Ir–$CH_2$), 2.78 (m, 2H, –$NCH_2$), 2.67 (m, 4H, –$CH(CH_3)_2$), 2.53 (m, 2H, –$NCH_2$), 2.44 (s, 3H, –$NCH_3$), 2.26 (s, 6H, –$N(CH_3)_2$), 2.25 (s, 6H, Ar–$CH_3$), 1.42 (dvt, 6H, –$CH(CH_3)_2$), 1.32 (m, 12H, –$CH(CH_3)_2$), 1.19 (dvt, 6H, –$CH(CH_3)_2$), 0.95 (d, $^2J_{PH} = 6.6$ Hz, 9H, –$P(CH_3)_3$), –11.61 (dt, $^2J_{PH(trans)} = 140$ Hz, $^2J_{PH(cis)} = 19.8$ Hz, 1H, Ir–$H$).

$^{13}C$ ($^1H$) NMR (C$_6$D$_6$): 162.5 (m), 131.7, 131.1, 129.7, 128.9, 126.0, 123.5, 115.9, 60.5, 60.1, 46.8, 45.6, 30.4, 27.9, 21.2, 21.0, 19.9, 19.6, 19.4, 18.0, 17.8, 16.5. $^{31}P$ ($^1H$) NMR (C$_6$D$_6$): 14.9 (d, $^2J_{PP} = 17$ Hz, 2P, Ir–($PNP$)), –53.8 (br, 1P, Ir–$P(CH_3)_3$). Anal. Calcd. for C$_{35}$H$_{65}$IrN$_3$P$_3$: C, 51.70; H, 8.06; N, 5.17. Found: C, 51.59; H, 8.20; N, 5.11.
Preparation of Complex (5). Aminocarbene 2 (ca. 10 mg) was dissolved in C₆D₆ (700 µL) and transferred to a resealable NMR tube. The solution was frozen and the headspace evacuated and backfilled with carbon monoxide (1 atm). The solution was warmed to room temperature and allowed to react for 12 h, then heated at 70 °C for 2 h to ensure complete conversion to 5. Complex 5 was not isolated, but its identity was confirmed by NMR, IR, and comparison to the analogous complex 4. ¹H NMR (C₆D₆): δ 7.71 (dt, J₁ = 8.1 Hz, J₂ = 2.1 Hz, 2H, Ar–H), 6.94 (m, 2H, Ar–H), 6.75 (dd, J₁ = 8.7 Hz, J₂ = 1.8 Hz, 2H, Ar–H), 3.25 (t, JₚH = 4.2 Hz, 2H, Ir–C₂H), 2.74 – 2.66 (m, 2H, –NCH₂), 2.58 – 2.40 (m, 6H, –C₃H(CH₃)₂ and –NCH₂), 2.36 (s, 3H, –NCH₃), 2.21 (s, 6H, –N(CH₃)₂), 2.20 (s, 6H, Ar–H), 1.36 – 1.03 (m, 24H, –CH(CH₃)₂), 6.90 (vt, 2H, Ar–H), 6.37 (dd, JₚH = 16.8 Hz, JₚH = 2.1 Hz, 1H, –NC(H)O′Bu), 2.70 (septet, JₚHH = 6.3 Hz, 1H, –CH(CH₃)₂), 2.31 (septet, JₚHH = 7.0 Hz, 1H, –CH(CH₃)₂), 2.19 (m, 2H, –CH(CH₃)₂), 2.13 (s, 3H, Ar–CH₃), 2.12 (s, 3H, Ar–CH₃), 1.49 – 1.22 (m, 12H, –

Preparation of Complex (6). (PNP)Ir=C(H)O′Bu (1) (54.4 mg, 0.0770 mmol) was dissolved in toluene (10 mL) and transferred to a resealable flask. The solution was frozen and the headspace evacuated and backfilled with carbon monoxide (1 atm). As the solution melted a color change from purple to yellow was observed, and the reaction was allowed to continue with stirring for 16 h. Volatiles were removed in vacuo to afford a yellow film, and off-white crystals of 6 (26.2 mg, 45%) were isolated by slow evaporation of pentane from a concentrated solution at -35 °C. ¹H NMR (C₆D₆): δ 7.42 (d, J = 6.9 Hz, 1H, Ar–H), 7.38 – 7.28 (m, 2H, Ar–H), 7.27 – 7.20 (m, 1H, Ar–H), 6.90 (vt, 2H, Ar–H), 6.37 (dd, JₚH = 16.8 Hz, JₚH = 2.1 Hz, 1H, –NC(H)O′Bu), 2.70 (septet, JₚHH = 6.3 Hz, 1H, –CH(CH₃)₂), 2.31 (septet, JₚHH = 7.0 Hz, 1H, –CH(CH₃)₂), 2.19 (m, 2H, –CH(CH₃)₂), 2.13 (s, 3H, Ar–CH₃), 2.12 (s, 3H, Ar–CH₃), 1.49 – 1.22 (m, 12H, –
CH(CH₃)₂, 1.09 (s, 9H, –OC(CH₃)₃), 0.94 – 0.72 (m, 12H, –CH(CH₃)₂). ¹³C{¹H} NMR (C₆D₆): δ 188.1 (t, ²JₚC = 37 Hz, Ir–CO), 184.8 (t, ²JₚC = 8.7 Hz, Ir–CO). ³¹P{¹H} NMR: δ 17.2 (d, ²Jₚp = 95.3 Hz), 2.9 (d, ²Jₚp = 95.3 Hz). IR (THF, KBr, cm⁻¹) ν(CO(symmetric)): 1981; ν(CO(antisymmetric)): 1924. Anal. Calcd for C₃₃H₅₀IrNO₃P₂: C, 51.95; H, 6.61; N, 1.84. Found: C, 53.11, 53.05; H, 6.67, 6.73; N, 1.70, 1.83.

**Thermal Isomerization of Aminocarbene (2).** Aminocarbene 2 (ca. 10 mg) was dissolved in C₆D₆ and transferred to an NMR tube. The sealed sample was heated at 70 °C for 12 h and examined by NMR spectroscopy, revealing a mixture of 2ₐnti, 2ₕyn, and two cis-dihydrido isomers of 2. The ³¹P NMR chemical shifts of the cis-2 isomers were observed at δ 48.5 and 46.2 ppm. Each complex also exhibited a distinct carbene proton and two hydrides by ¹H NMR spectroscopy.

¹H NMR (cis-2 (major), C₆D₆): δ 11.92 (s, 1H, Ir=C(H)N), –12.81 (dt, J₁ = 21 Hz, J₂ = 5.4 Hz, 1H, Ir–H), –19.21 (br s, 1H, Ir–H).

¹H NMR (cis-2 (minor), C₆D₆): δ 11.87 (s, 1H, Ir=C(H)N), –12.46 (t, J₁ = 21 Hz, J₂ = 6 Hz, 1H, Ir–H), –19.38 (br s, 1H, Ir–H).