Supporting Information

Reversible Alkyl C-H Bond Activation, Alcohol Dehydrogenation and *Trans-Cis* Dihydride Isomerisation in Ruthenium N-Heterocyclic Carbene Complexes

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I. Synthetic, Spectroscopic and Analytical Data

$Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (1).

Toluene (20 mL) was added to IEt_2Me_2 (700 mg, 4.60 mmol) and $Ru(PPh_3)_3(CO)(H)_2$ (1.4 g, 1.53 mmol) in a schlenk flask under argon. The mixture was heated at 70 °C with stirring for 20 hours. The volatiles were removed *in vacuo* and the red/brown oily residue was washed with ethanol (1 x 20 mL), left to form a precipitate and then filtered. The solid was dissolved in benzene (5 mL) and heated at 70 °C for 1 hour. The volatiles were removed *in vacuo* and the resulting solid dissolved in THF and layered with hexane affording $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (**1**) as a white crystalline solid. Yield 600 mg, 48%. ^{1}H (THF-d_8, 298K): δ 7.62-7.48 (m, 12H, PPh_3), 7.25-7.07 (m, 18H, PPh_3), 3.69 (q, J_{HH} = 6.6 Hz, 2H, CH_2), 3.28 (q, J_{HH} = 6.6 Hz, 2H, CH_2), 2.00 (s, 3H, im-CH_3), 1.72 (s, 3H, im-CH_3), 1.01 (t, J_{HH} = 6.6 Hz, 3H, CH_3), 0.34 (t, J_{HH} = 6.6 Hz, 3H, CH_3), -6.38 (dt, J_{HP} = 26.3 Hz, J_{HH} = 5.5 Hz, 1H, Ru-*H*), -9.99 (dt, J_{HP} = 24.7 Hz, J_{HH} = 5.5 Hz, 1H, Ru-*H*). ^{31}P{^{1}H} (THF-d_8, 298 K): δ 63.7 (s, PPh_3). ^{13}C{^{1}H}(THF-d_8, 298 K): δ 208.3 (t, J_{CP} = 9.2 Hz, *C*O), 191.1 (t, J_{CP} = 8.3 Hz, Ru-*C*(carbene)), 141.6 (t, J_{CP} = 19.3 Hz, PPh_3), 134.6 (t, J_{CP} = 6.4 Hz, PPh_3), 128.6 (s, PPh_3), 127.6 (t, J_{CP} = 4.6 Hz, PPh_3), 124.2 (s, im-*C*), 124.1 (s, im-*C*), 43.9 (s, *C*H_2, Et), 43.7 (s, *C*H_2, Et), 15.9 (s, im-*C*H_3), 14.2 (s, im-*C*H_3), 9.6 (s, *C*H_3, Et), 9.4 (s, *C*H_3, Et). IR (nujol, cm^{-1}): 1913 (ν_{CO}). Analysis for $RuC_{46}H_{48}N_2OP_2$ [found (calculated)]: C, 68.6 (68.39); H, 6.08 (5.99); N, 3.46 (3.47).

$Ru(IEt_2Me_2)'(PPh_3)_2(CO)H$ (3)

Trimethylvinylsilane (100 equivalents) was added to $Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2$ (**1**) (15 mg) dissolved in d_8-THF (0.6 mL). The sample was heated at 50 °C for 16 hours. ^{31}P{^{1}H} NMR spectroscopy indicated complete conversion to the C-H activated complex **3**. The solvent was

removed *in vacuo* affording a yellow solid. Yellow crystals for x-ray analysis were grown by layering a THF solution with hexane. ^{1}H (benzene-d_6, 298 K): δ 7.96-7.84 (m, 12H, PPh_3), 7.11-6.87 (m, 18H, PPh_3), 3.28 (q, J_{HH} = 7.1 Hz, 2H, CH_2-CH_3), 2.67-2.78 (m, 2H CH_2), 1.50 (s, 3H, im-CH_3), 1.34(s, 3H, im-CH_3), 1.28-1.16 (m, 2H, CH_2), 0.73 (t, J_{HH} = 7.1 Hz, 3H, CH_3), -7.01 (t, J_{HP} = 23.1 Hz, 1H, Ru-*H*). ^{31}P{^{1}H} (benzene-d_6, 298 K): δ 61.1 (s, PPh_3). ^{13}C{^{1}H} (benzene-d_6, 298 K): δ 206.4 (t, J_{CP} = 11.7 Hz, *C*O), 191.7 (t, J_{CP} = 8.8 Hz, Ru-*C*(carbene)), 139.3 (t, J_{CP} = 19.0 Hz, PPh_3), 134.3 (t, J_{CP} = 5.9 Hz, PPh_3), 128.4 (s, PPh_3), 127.6 (t, J_{CP} = 4.4 Hz, PPh_3), 122.3 (m, 2 x im-*C*), 50.2 (s, *C*H_2-CH_2-Ru), 42.9 (s, *C*H_2, Et), 15.7 (s, *C*H_3, Et), 9.5 (s, im-*C*H_3), 8.9 (s, im-*C*H_3), 8.3 (t, J_{CP} = 11.0 Hz, *C*H_2-Ru). IR (nujol, cm^{-1}): 1884 (ν_{CO}). Analysis for $RuC_{46}H_{46}N_2OP_2$ [found (calculated)]: C, 68.7 (68.56); H, 6.38 (5.75); N, 3.20 (3.48).

***trans*-Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$ (4).**

Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$ (**1**) was stirred in ethanol for 16 hours at room temperature. The resulting green precipitate was filtered and washed with THF, affording *trans*-Ru(IEt$_2$Me$_2$)(PPh$_3$)$_2$(CO)H$_2$ (**4**) as a white solid. ^{1}H (pyridine-d_5, 298 K): δ 7.51-7.40 (m, 12 H, PPh_3), 7.39-7.30 (m, 18H, PPh_3) 3.93 (q, J_{HH} = 7.1 Hz, 4H, CH_2), 1.76 (s, 6H, im-CH_3), 0.67 (t, J_{HH} = 7.1 Hz, 6H, CH_3), -4.90 (t, J_{HP} = 20.3 Hz, 2H, Ru-*H*). ^{31}P{^{1}H} (pyridine-d_5, 298 K): δ 63.2 (s, PPh_3). ^{13}C{^{1}H}(pyridine-d_5, 298 K): δ 209.9 (*CO**), 183.6 (Ru-*C*(carbene)*), 139.5 (t, J_{CP} = 19.2 Hz, PPh_3), 134.3 (m, PPh_3), 128.6 (m, PPh_3), 127.3 (m, PPh_3), 124.4 (s, im-*C*), 43.2 (s, *C*H_2, Et), 14.3 (s, im-*C*H_3), 9.3 (s, *C*H_3, Et). IR (nujol, cm^{-1}): 1905 (ν_{CO}). Analysis for $RuC_{46}H_{48}N_2OP_2$ [found (calculated)]: C, 68.2 (68.39); H, 6.00 (5.99); N, 3.51 (3.47).

* Due to low solubility and rapid isomerisation, ^{13}C shifts obtained by ^{13}C-^{1}H HMBC spectroscopy.

II. X-ray Experimental Data.

III. Structural data for 1

Figure S-1. Molecular structure of **1**.

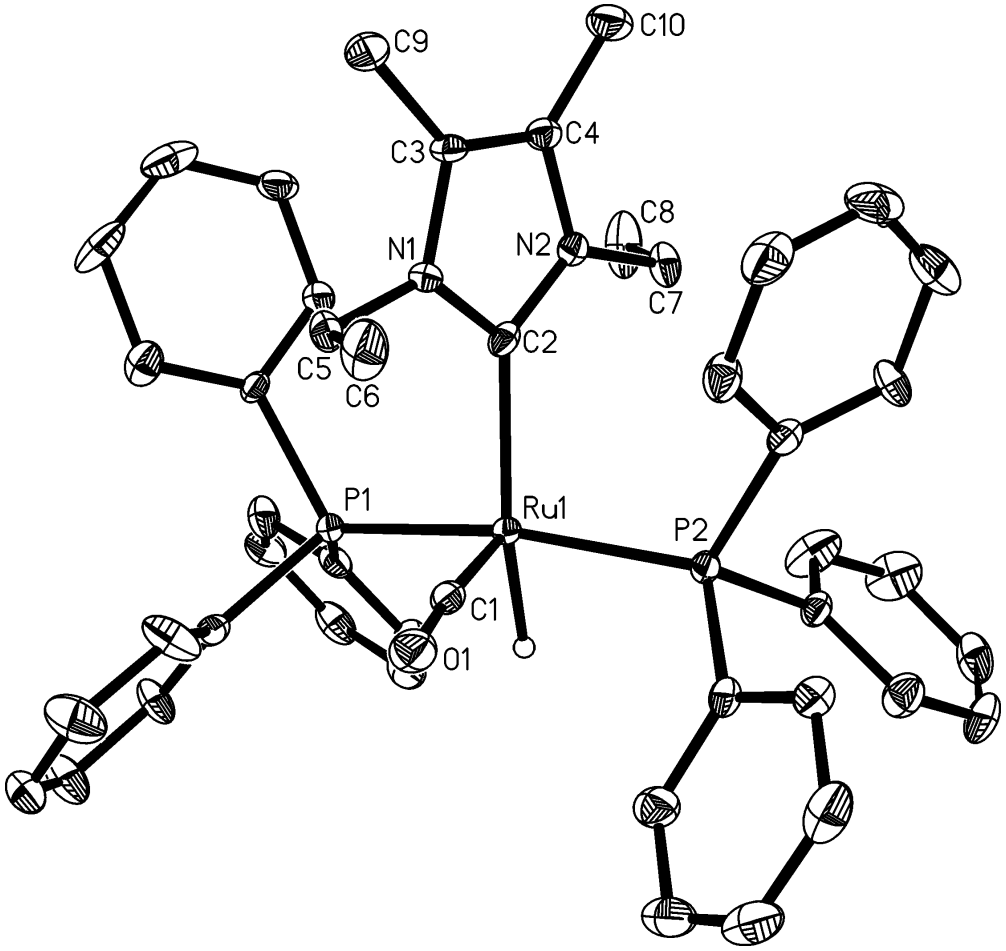

Table S-1. Crystal data and structure refinement for $[Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2]$ **1**.

Identification code	h04mkw1
Empirical formula	$C_{46}H_{48}N_2OP_2Ru$
Formula weight	807.87
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	Cc
Unit cell dimensions	a = 23.5760(2)Å α = 90°
	b = 9.9740(1)Å β = 113.239(1)^o
	c = 18.2220(2)Å γ = 90°
Volume	3937.20(7) Å^3
Z	4
Density (calculated)	1.363 Mg/m^3
Absorption coefficient	0.517 mm^{-1}
F(000)	1680
Crystal size	0.15 x 0.10 x 0.10 mm
Theta range for data collection	3.58 to 27.49^o
Index ranges	-30<=h<=28; -12<=k<=12; -23<=l<=23
Reflections collected	32590
Independent reflections	8871 [R(int) = 0.0583]
Reflections observed (>2σ)	7674
Data Completeness	0.997
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8871 / 16 / 503
Goodness-of-fit on F^2	1.033
Final R indices [I>2σ(I)]	R1 = 0.0355 wR2 = 0.0735
R indices (all data)	R1 = 0.0470 wR2 = 0.0773
Absolute structure parameter	0.21(2)
Largest diff. peak and hole	0.373 and -0.425 eÅ^{-3}

Notes: Ru, C1, and O1 disordered in ratio 80:20 with their primed labelled counterparts. H1 are refined at 1.6 Å from metal centres. No attempt made to locate the second hydride ligand because of disorder.

Table S-2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for [Ru(IEt_2Me_2)(PPh_3)$_2$(CO)H_2] **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Ru(1)	7255(1)	7902(1)	7552(1)	20(1)
P(1)	6311(1)	7671(1)	6467(1)	22(1)
P(2)	8255(1)	7629(1)	8464(1)	23(1)
O(1)	6805(2)	7517(4)	8893(2)	40(1)
N(1)	6906(2)	10946(3)	7653(2)	22(1)
N(2)	7647(2)	10899(3)	7261(2)	22(1)
C(1)	6966(2)	7721(5)	8371(2)	24(1)
C(2)	7278(2)	10070(2)	7478(3)	24(1)
C(3)	7046(2)	12285(4)	7559(2)	25(1)
C(4)	7516(2)	12252(4)	7321(2)	25(1)
C(5)	6429(2)	10615(5)	7940(2)	32(1)
C(6)	6649(2)	10758(6)	8852(3)	52(1)
C(7)	8135(2)	10481(5)	7004(2)	32(1)
C(8)	7938(2)	10427(6)	6117(3)	56(1)
C(9)	6676(2)	13441(4)	7657(3)	39(1)
C(10)	7873(2)	13371(5)	7167(3)	42(1)
C(11)	5937(2)	9268(4)	6028(2)	23(1)
C(12)	6274(2)	10105(4)	5742(2)	31(1)
C(13)	6077(2)	11409(4)	5498(3)	40(1)
C(14)	5535(3)	11863(5)	5538(3)	51(1)
C(15)	5185(3)	11032(5)	5784(3)	50(1)
C(16)	5389(2)	9721(5)	6036(2)	37(1)
C(17)	5701(2)	6793(4)	6669(2)	26(1)
C(18)	5345(2)	5761(5)	6186(3)	37(1)
C(19)	4895(2)	5121(6)	6360(3)	50(1)
C(20)	4778(2)	5492(5)	7013(3)	42(1)
C(21)	5101(3)	6530(5)	7478(3)	55(1)
C(22)	5560(2)	7160(5)	7314(2)	48(1)
C(23)	6276(2)	6758(4)	5574(2)	28(1)
C(24)	5851(2)	7053(5)	4819(2)	36(1)
C(25)	5800(2)	6294(5)	4159(3)	40(1)
C(26)	6184(2)	5197(5)	4261(3)	44(1)
C(27)	6615(2)	4876(5)	5012(3)	43(1)
C(28)	6668(2)	5669(4)	5667(2)	36(1)
C(29)	8652(2)	9198(4)	8905(2)	26(1)
C(30)	8328(2)	10095(5)	9188(3)	38(1)
C(31)	8545(3)	11379(5)	9403(3)	54(1)
C(32)	9077(3)	11799(5)	9345(3)	56(1)
C(33)	9411(2)	10899(5)	9093(2)	47(1)
C(34)	9210(2)	9613(4)	8888(2)	33(1)
C(35)	8302(2)	6678(4)	9342(2)	28(1)
C(36)	7953(2)	5504(4)	9232(3)	40(1)
C(37)	7982(2)	4744(5)	9874(3)	48(1)
C(38)	8349(3)	5115(5)	10633(3)	53(2)

C(39)	8704(2)	6236(6)	10757(3)	52(2)
C(40)	8691(2)	7041(5)	10129(2)	34(1)
C(41)	8854(2)	6763(4)	8219(2)	26(1)
C(42)	9276(2)	5900(5)	8754(3)	41(1)
C(43)	9734(2)	5304(5)	8566(3)	48(1)
C(44)	9780(2)	5564(5)	7860(3)	45(1)
C(45)	9369(3)	6434(5)	7328(3)	55(1)
C(46)	8895(2)	6995(5)	7500(3)	51(1)
Ru(1A)	7331(1)	7923(2)	7286(1)	18(1)
O(1A)	7768(5)	7623(12)	5961(6)	22(3)
C(1A)	7603(7)	7727(17)	6492(9)	14(3)

Table S-3. Bond lengths [Å] and angles [°] for [Ru(IEt_2Me_2)(PPh_3)$_2$(CO)H_2] **1**.

Ru(1)-C(1)	1.878(4)	Ru(1)-C(2)	2.168(2)
Ru(1)-P(2)	2.3034(11)	Ru(1)-P(1)	2.3329(11)
P(1)-C(23)	1.837(3)	P(1)-C(17)	1.842(4)
P(1)-C(11)	1.843(4)	P(1)-Ru(1A)	2.289(3)
P(2)-C(35)	1.826(4)	P(2)-C(29)	1.837(4)
P(2)-C(41)	1.853(4)	P(2)-Ru(1A)	2.398(3)
O(1)-C(1)	1.173(4)	N(1)-C(2)	1.362(4)
N(1)-C(3)	1.402(5)	N(1)-C(5)	1.453(4)
N(2)-C(2)	1.368(5)	N(2)-C(4)	1.399(5)
N(2)-C(7)	1.462(4)	C(2)-Ru(1A)	2.181(3)
C(3)-C(4)	1.341(3)	C(3)-C(9)	1.499(5)
C(4)-C(10)	1.488(6)	C(5)-C(6)	1.540(6)
C(7)-C(8)	1.497(6)	C(11)-C(16)	1.374(5)
C(11)-C(12)	1.388(5)	C(12)-C(13)	1.393(6)
C(13)-C(14)	1.384(7)	C(14)-C(15)	1.364(7)
C(15)-C(16)	1.405(6)	C(17)-C(22)	1.391(5)
C(17)-C(18)	1.399(6)	C(18)-C(19)	1.377(5)
C(19)-C(20)	1.375(6)	C(20)-C(21)	1.363(7)
C(21)-C(22)	1.382(6)	C(23)-C(24)	1.377(6)
C(23)-C(28)	1.392(6)	C(24)-C(25)	1.386(6)
C(25)-C(26)	1.385(7)	C(26)-C(27)	1.382(7)
C(27)-C(28)	1.395(6)	C(29)-C(34)	1.392(5)
C(29)-C(30)	1.401(5)	C(30)-C(31)	1.377(7)
C(31)-C(32)	1.366(8)	C(32)-C(33)	1.385(7)
C(33)-C(34)	1.367(6)	C(35)-C(36)	1.400(6)
C(35)-C(40)	1.411(6)	C(36)-C(37)	1.373(6)
C(37)-C(38)	1.361(8)	C(38)-C(39)	1.362(8)
C(39)-C(40)	1.389(6)	C(41)-C(46)	1.372(5)
C(41)-C(42)	1.384(6)	C(42)-C(43)	1.388(6)
C(43)-C(44)	1.358(6)	C(44)-C(45)	1.375(7)
C(45)-C(46)	1.392(6)	Ru(1A)-C(1A)	1.809(13)
O(1A)-C(1A)	1.182(16)		
C(1)-Ru(1)-C(2)	99.85(17)	C(1)-Ru(1)-P(2)	90.30(14)
C(2)-Ru(1)-P(2)	96.83(15)	C(1)-Ru(1)-P(1)	98.04(14)
C(2)-Ru(1)-P(1)	94.88(15)	P(2)-Ru(1)-P(1)	164.25(3)
C(23)-P(1)-C(17)	100.15(17)	C(23)-P(1)-C(11)	101.43(17)
C(17)-P(1)-C(11)	102.66(17)	C(23)-P(1)-Ru(1A)	107.50(14)
C(17)-P(1)-Ru(1A)	128.62(14)	C(11)-P(1)-Ru(1A)	112.80(15)
C(23)-P(1)-Ru(1)	119.61(14)	C(17)-P(1)-Ru(1)	115.88(13)
C(11)-P(1)-Ru(1)	114.51(14)	Ru(1A)-P(1)-Ru(1)	14.36(4)
C(35)-P(2)-C(29)	102.40(18)	C(35)-P(2)-C(41)	100.38(17)
C(29)-P(2)-C(41)	101.40(18)	C(35)-P(2)-Ru(1)	112.58(13)
C(29)-P(2)-Ru(1)	114.50(14)	C(41)-P(2)-Ru(1)	122.83(13)
C(35)-P(2)-Ru(1A)	124.53(14)	C(29)-P(2)-Ru(1A)	114.43(14)
C(41)-P(2)-Ru(1A)	110.58(13)	Ru(1)-P(2)-Ru(1A)	13.97(4)
C(2)-N(1)-C(3)	112.2(3)	C(2)-N(1)-C(5)	126.8(3)

C(3)-N(1)-C(5)	120.9(3)	C(2)-N(2)-C(4)	112.1(2)
C(2)-N(2)-C(7)	126.2(3)	C(4)-N(2)-C(7)	121.7(3)
O(1)-C(1)-Ru(1)	175.1(4)	N(1)-C(2)-N(2)	102.82(17)
N(1)-C(2)-Ru(1)	126.2(2)	N(2)-C(2)-Ru(1)	130.9(2)
N(1)-C(2)-Ru(1A)	138.6(3)	N(2)-C(2)-Ru(1A)	117.6(2)
Ru(1)-C(2)-Ru(1A)	15.30(4)	C(4)-C(3)-N(1)	106.3(4)
C(4)-C(3)-C(9)	130.7(4)	N(1)-C(3)-C(9)	122.8(3)
C(3)-C(4)-N(2)	106.6(4)	C(3)-C(4)-C(10)	130.0(5)
N(2)-C(4)-C(10)	123.4(3)	N(1)-C(5)-C(6)	112.8(3)
N(2)-C(7)-C(8)	114.1(3)	C(16)-C(11)-C(12)	119.0(4)
C(16)-C(11)-P(1)	124.8(3)	C(12)-C(11)-P(1)	115.8(3)
C(11)-C(12)-C(13)	120.9(4)	C(14)-C(13)-C(12)	119.1(4)
C(15)-C(14)-C(13)	120.6(4)	C(14)-C(15)-C(16)	119.9(4)
C(11)-C(16)-C(15)	120.3(4)	C(22)-C(17)-C(18)	116.2(3)
C(22)-C(17)-P(1)	120.7(3)	C(18)-C(17)-P(1)	123.1(3)
C(19)-C(18)-C(17)	121.4(4)	C(20)-C(19)-C(18)	120.7(5)
C(21)-C(20)-C(19)	119.3(4)	C(20)-C(21)-C(22)	120.2(4)
C(21)-C(22)-C(17)	122.1(4)	C(24)-C(23)-C(28)	118.3(4)
C(24)-C(23)-P(1)	122.7(3)	C(28)-C(23)-P(1)	118.9(3)
C(23)-C(24)-C(25)	122.0(4)	C(26)-C(25)-C(24)	119.1(5)
C(27)-C(26)-C(25)	120.2(4)	C(26)-C(27)-C(28)	119.9(4)
C(23)-C(28)-C(27)	120.4(4)	C(34)-C(29)-C(30)	118.4(4)
C(34)-C(29)-P(2)	124.5(3)	C(30)-C(29)-P(2)	116.6(3)
C(31)-C(30)-C(29)	120.2(4)	C(32)-C(31)-C(30)	120.8(5)
C(31)-C(32)-C(33)	119.1(5)	C(34)-C(33)-C(32)	121.3(4)
C(33)-C(34)-C(29)	120.0(4)	C(36)-C(35)-C(40)	118.0(4)
C(36)-C(35)-P(2)	118.8(3)	C(40)-C(35)-P(2)	123.2(3)
C(37)-C(36)-C(35)	120.7(5)	C(38)-C(37)-C(36)	120.9(5)
C(37)-C(38)-C(39)	119.6(4)	C(38)-C(39)-C(40)	121.7(5)
C(39)-C(40)-C(35)	119.0(5)	C(46)-C(41)-C(42)	118.4(4)
C(46)-C(41)-P(2)	119.9(3)	C(42)-C(41)-P(2)	121.7(3)
C(41)-C(42)-C(43)	120.3(4)	C(44)-C(43)-C(42)	120.8(5)
C(43)-C(44)-C(45)	119.5(4)	C(44)-C(45)-C(46)	119.9(4)
C(41)-C(46)-C(45)	120.9(4)	C(1A)-Ru(1A)-C(2)	107.2(5)
C(1A)-Ru(1A)-P(1)	94.5(5)	C(2)-Ru(1A)-P(1)	95.77(17)
C(1A)-Ru(1A)-P(2)	102.7(5)	C(2)-Ru(1A)-P(2)	93.76(17)
P(1)-Ru(1A)-P(2)	156.95(9)	O(1A)-C(1A)-Ru(1A)	178.3(15)

Symmetry transformations used to generate equivalent atoms:

Table S-4. Anisotropic displacement parameters ($Å^2$ x 10^3) for $[Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2]$ **1**. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Ru(1)	18(1)	15(1)	24(1)	1(1)	6(1)	0(1)
P(1)	17(1)	19(1)	29(1)	2(1)	6(1)	0(1)
P(2)	18(1)	20(1)	28(1)	-1(1)	6(1)	1(1)
O(1)	43(2)	41(2)	42(2)	10(2)	24(2)	5(1)
N(1)	23(2)	18(2)	25(1)	3(1)	10(1)	-2(1)
N(2)	21(2)	24(2)	23(1)	1(1)	9(1)	2(1)
C(1)	24(2)	22(2)	24(2)	3(2)	8(2)	3(2)
C(2)	22(1)	21(1)	23(1)	-4(2)	4(1)	5(2)
C(3)	29(2)	14(2)	30(2)	-1(1)	11(2)	0(1)
C(4)	27(2)	23(2)	26(2)	4(2)	11(2)	1(2)
C(5)	20(2)	37(2)	38(2)	8(2)	11(2)	-2(2)
C(6)	41(3)	77(3)	47(3)	21(2)	27(2)	8(2)
C(7)	22(2)	42(2)	30(2)	-12(2)	10(2)	-3(2)
C(8)	31(2)	107(4)	32(2)	-18(2)	17(2)	2(2)
C(9)	38(2)	24(2)	57(2)	-10(2)	23(2)	3(2)
C(10)	45(3)	30(2)	59(3)	6(2)	28(2)	-3(2)
C(11)	19(2)	21(2)	25(2)	2(1)	3(2)	5(2)
C(12)	23(2)	27(2)	37(2)	5(2)	6(2)	-2(2)
C(13)	38(3)	26(2)	41(2)	12(2)	-1(2)	-6(2)
C(14)	72(4)	28(3)	38(2)	5(2)	6(2)	16(2)
C(15)	61(3)	58(3)	36(2)	21(2)	23(2)	42(3)
C(16)	35(2)	48(3)	32(2)	8(2)	20(2)	10(2)
C(17)	27(2)	23(2)	31(2)	6(1)	13(2)	6(2)
C(18)	31(2)	41(2)	42(2)	-16(2)	18(2)	-19(2)
C(19)	41(3)	52(3)	58(3)	-12(2)	21(2)	-21(2)
C(20)	34(3)	44(3)	51(3)	7(2)	19(2)	-7(2)
C(21)	80(3)	53(3)	52(3)	-3(2)	46(3)	-15(2)
C(22)	67(3)	44(2)	39(2)	-13(2)	29(2)	-30(2)
C(23)	28(2)	25(2)	39(2)	-6(2)	20(2)	-6(2)
C(24)	25(2)	45(3)	36(2)	-9(2)	8(2)	-5(2)
C(25)	46(3)	36(3)	37(2)	-7(2)	17(2)	-11(2)
C(26)	46(3)	48(3)	46(2)	-19(2)	27(2)	-20(2)
C(27)	42(3)	35(2)	62(3)	-10(2)	33(2)	-1(2)
C(28)	30(2)	38(2)	40(2)	1(2)	15(2)	5(2)
C(29)	26(2)	24(2)	25(2)	0(1)	6(2)	6(2)
C(30)	28(2)	38(3)	39(2)	-13(2)	4(2)	4(2)
C(31)	54(3)	38(3)	51(3)	-19(2)	-1(2)	13(2)
C(32)	72(4)	31(3)	40(2)	-4(2)	-4(2)	-18(2)
C(33)	53(3)	54(3)	31(2)	-8(2)	14(2)	-29(2)
C(34)	28(2)	40(2)	30(2)	-14(2)	10(2)	-15(2)
C(35)	20(2)	30(2)	33(2)	1(2)	11(2)	5(2)
C(36)	42(2)	31(2)	52(2)	3(2)	25(2)	5(2)
C(37)	55(3)	32(2)	74(3)	11(2)	44(3)	7(2)
C(38)	66(4)	43(3)	67(3)	23(2)	46(3)	21(3)

C(39)	42(3)	73(4)	39(2)	12(2)	15(2)	17(3)
C(40)	32(3)	31(3)	39(2)	4(2)	13(2)	4(2)
C(41)	21(2)	24(2)	28(2)	-2(1)	5(2)	5(2)
C(42)	37(2)	45(2)	44(2)	6(2)	18(2)	10(2)
C(43)	29(2)	54(3)	57(3)	6(2)	12(2)	20(2)
C(44)	28(2)	51(3)	61(3)	-19(2)	23(2)	-1(2)
C(45)	76(3)	56(3)	51(3)	-2(2)	44(3)	17(2)
C(46)	74(3)	49(2)	39(2)	4(2)	33(2)	28(2)
Ru(1A)	16(1)	18(1)	20(1)	-1(1)	6(1)	-1(1)
O(1A)	22(4)	24(4)	23(3)	-2(2)	11(3)	-2(2)
C(1A)	11(4)	11(4)	17(4)	-2(3)	2(3)	-2(3)

Table S-5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for $[Ru(IEt_2Me_2)(PPh_3)_2(CO)H_2]$ **1**.

Atom	x	y	z	U(eq)
H(5A)	6291	9681	7787	38
H(5B)	6070	11211	7678	38
H(6A)	6310	10529	9013	78
H(6B)	6780	11685	9008	78
H(6C)	6998	10152	9116	78
H(7A)	8283	9582	7228	38
H(7B)	8486	11112	7229	38
H(8A)	8288	10145	5990	83
H(8B)	7799	11317	5889	83
H(8C)	7599	9784	5889	83
H(9A)	6869	14285	7603	58
H(9B)	6662	13399	8187	58
H(9C)	6255	13394	7246	58
H(10A)	7742	14223	7317	63
H(10B)	7797	13390	6598	63
H(10C)	8314	13236	7484	63
H(12)	6644	9785	5712	37
H(13)	6311	11978	5306	48
H(14)	5406	12762	5394	61
H(15)	4804	11338	5786	60
H(16)	5147	9146	6211	44
H(18)	5414	5496	5727	44
H(19)	4664	4415	6026	60
H(20)	4476	5031	7140	51
H(21)	5011	6821	7917	66
H(22)	5786	7867	7653	57
H(24)	5585	7801	4748	44
H(25)	5505	6522	3643	48
H(26)	6152	4664	3814	53
H(27)	6874	4116	5083	51
H(28)	6974	5465	6180	43
H(30)	7957	9818	9232	46
H(31)	8322	11981	9594	65
H(32)	9217	12695	9475	67
H(33)	9786	11181	9063	56
H(34)	9452	9003	8733	40
H(36)	7693	5229	8707	47
H(37)	7742	3949	9788	57
H(38)	8357	4594	11074	63
H(39)	8968	6474	11288	62
H(40)	8940	7823	10227	41
H(42)	9253	5716	9253	49
H(43)	10019	4708	8936	58
H(44)	10093	5147	7735	54
H(45)	9410	6653	6843	66
H(46)	8596	7545	7114	61

H(1)	7336(19)	6344(8)	7360(20)	50

IV. Structural data for 3.

Figure S-2. Molecular structure of **3**.

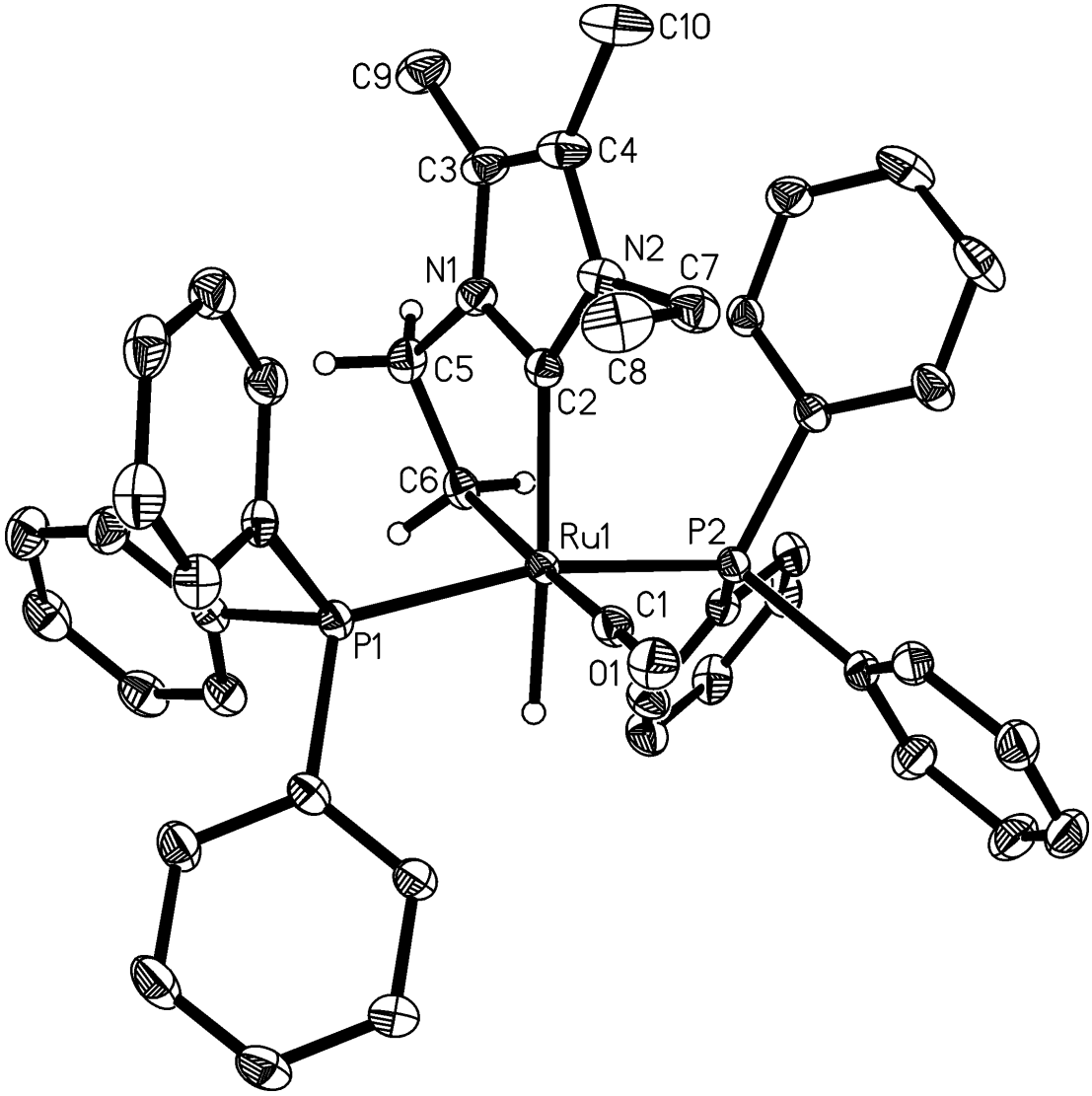

Table S-6. Crystal data and structure refinement for $[Ru(IEt_2Me_2)'(PPh_3)_2(CO)H]$ **3**.

Identification code	h04mkw2
Empirical formula	$C_{46}H_{46}N_2OP_2Ru$
Formula weight	805.86
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	a = 16.9680(1)Å α = 90°
	b = 10.5800(1)Å β = 109.720(1)^o
	c = 23.1530(2)Å γ = 90°
Volume	3912.60(6) Å^3
Z	4
Density (calculated)	1.368 Mg/m^3
Absorption coefficient	0.520 mm^{-1}
F(000)	1672
Crystal size	0.15 x 0.15 x 0.10 mm
Theta range for data collection	3.85 to 27.47^o
Index ranges	-22<=h<=22; -13<=k<=13; -29<=l<=30
Reflections collected	58667
Independent reflections	8901 [R(int) = 0.0497]
Reflections observed (>2σ)	7511
Data Completeness	0.995
Absorption correction	None
Max. and min. transmission	0.9498 and 0.9260
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8901 / 5 / 484
Goodness-of-fit on F^2	1.051
Final R indices [I>2σ(I)]	R1 = 0.0276 wR2 = 0.0629
R indices (all data)	R1 = 0.0375 wR2 = 0.0671
Largest diff. peak and hole	0.356 and -0.642 eÅ^{-3}

Notes: **H1, H5A, H5B, H6A and H6B located and refined at fixed distances of 1.6Å (H1 – Ru1) and 0.89Å for the subsequent pairs, from the relevant parent carbon atom.**

Table S-7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for [Ru(IEt_2Me_2)′(PPh_3)$_2$(CO)H] **3**.U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Atom	x	y	z	U(eq)
Ru(1)	2379(1)	384(1)	7452(1)	23(1)
P(1)	3313(1)	12(1)	8433(1)	25(1)
P(2)	1362(1)	192(1)	6484(1)	24(1)
O(1)	3879(1)	403(1)	7024(1)	43(1)
N(2)	2472(1)	3406(1)	7278(1)	31(1)
N(1)	1743(1)	2773(1)	7815(1)	29(1)
C(1)	3289(1)	379(2)	7170(1)	29(1)
C(2)	2233(1)	2338(2)	7499(1)	26(1)
C(3)	1692(1)	4082(2)	7807(1)	36(1)
C(4)	2152(1)	4488(2)	7468(1)	37(1)
C(5)	1373(1)	1857(2)	8125(1)	34(1)
C(6)	1339(1)	561(2)	7820(1)	29(1)
C(7)	3008(1)	3427(2)	6900(1)	40(1)
C(8)	3927(1)	3571(2)	7283(1)	54(1)
C(9)	1185(1)	4799(2)	8114(1)	48(1)
C(10)	2304(2)	5787(2)	7277(1)	57(1)
C(11)	898(1)	1696(2)	6126(1)	26(1)
C(12)	516(1)	2459(2)	6447(1)	31(1)
C(13)	258(1)	3673(2)	6257(1)	40(1)
C(14)	381(1)	4149(2)	5736(1)	51(1)
C(15)	722(1)	3390(2)	5398(1)	54(1)
C(16)	976(1)	2165(2)	5588(1)	39(1)
C(17)	432(1)	-757(2)	6431(1)	28(1)
C(18)	-365(1)	-459(2)	6036(1)	35(1)
C(19)	-1039(1)	-1248(2)	5995(1)	43(1)
C(20)	-923(1)	-2347(2)	6334(1)	43(1)
C(21)	-132(1)	-2658(2)	6720(1)	43(1)
C(22)	538(1)	-1861(2)	6778(1)	37(1)
C(23)	1688(1)	-541(2)	5878(1)	30(1)
C(24)	2359(1)	-21(2)	5738(1)	35(1)
C(25)	2620(1)	-533(2)	5283(1)	44(1)
C(26)	2219(1)	-1582(2)	4961(1)	49(1)
C(27)	1562(2)	-2113(2)	5092(1)	51(1)
C(28)	1290(1)	-1595(2)	5547(1)	41(1)
C(29)	3990(1)	-1389(2)	8523(1)	30(1)
C(30)	4413(1)	-1876(2)	9107(1)	41(1)
C(31)	4920(1)	-2936(2)	9179(1)	49(1)
C(32)	5020(1)	-3517(2)	8675(1)	42(1)
C(33)	4607(1)	-3052(2)	8098(1)	38(1)
C(34)	4088(1)	-2001(2)	8022(1)	33(1)
C(35)	4071(1)	1269(2)	8798(1)	29(1)
C(36)	3773(1)	2498(2)	8799(1)	35(1)
C(37)	4312(1)	3492(2)	9045(1)	41(1)
C(38)	5164(1)	3279(2)	9294(1)	44(1)

C(39)	5472(1)	2074(2)	9297(1)	44(1)
C(40)	4933(1)	1074(2)	9051(1)	37(1)
C(41)	2863(1)	-375(2)	9034(1)	30(1)
C(42)	2938(1)	361(2)	9541(1)	40(1)
C(43)	2555(2)	-13(2)	9963(1)	50(1)
C(44)	2114(1)	-1114(2)	9882(1)	48(1)
C(45)	2034(1)	-1860(2)	9378(1)	44(1)
C(46)	2403(1)	-1489(2)	8957(1)	37(1)

Table S-8. Bond lengths [Å] and angles [°] for [Ru(IEt_2Me_2)′(PPh_3)$_2$(CO)H] **3**.

Ru(1)-C(1)	1.8691(18)	Ru(1)-C(2)	2.0893(18)
Ru(1)-C(6)	2.2107(17)	Ru(1)-P(1)	2.3217(5)
Ru(1)-P(2)	2.3315(5)	P(1)-C(29)	1.8445(18)
P(1)-C(41)	1.8450(18)	P(1)-C(35)	1.8456(18)
P(2)-C(17)	1.8391(18)	P(2)-C(11)	1.8428(17)
P(2)-C(23)	1.8434(18)	O(1)-C(1)	1.160(2)
N(2)-C(2)	1.357(2)	N(2)-C(4)	1.400(2)
N(2)-C(7)	1.460(2)	N(1)-C(2)	1.360(2)
N(1)-C(3)	1.387(2)	N(1)-C(5)	1.466(2)
C(3)-C(4)	1.350(3)	C(3)-C(9)	1.496(3)
C(4)-C(10)	1.493(3)	C(5)-C(6)	1.535(3)
C(7)-C(8)	1.519(3)	C(11)-C(16)	1.390(3)
C(11)-C(12)	1.396(2)	C(12)-C(13)	1.380(3)
C(13)-C(14)	1.386(3)	C(14)-C(15)	1.378(3)
C(15)-C(16)	1.389(3)	C(17)-C(18)	1.389(3)
C(17)-C(22)	1.395(3)	C(18)-C(19)	1.392(3)
C(19)-C(20)	1.378(3)	C(20)-C(21)	1.378(3)
C(21)-C(22)	1.384(3)	C(23)-C(28)	1.392(3)
C(23)-C(24)	1.398(3)	C(24)-C(25)	1.382(3)
C(25)-C(26)	1.382(3)	C(26)-C(27)	1.371(3)
C(27)-C(28)	1.397(3)	C(29)-C(34)	1.386(3)
C(29)-C(30)	1.397(3)	C(30)-C(31)	1.388(3)
C(31)-C(32)	1.379(3)	C(32)-C(33)	1.373(3)
C(33)-C(34)	1.393(3)	C(35)-C(40)	1.395(3)
C(35)-C(36)	1.396(3)	C(36)-C(37)	1.384(3)
C(37)-C(38)	1.383(3)	C(38)-C(39)	1.377(3)
C(39)-C(40)	1.390(3)	C(41)-C(42)	1.378(3)
C(41)-C(46)	1.392(3)	C(42)-C(43)	1.401(3)
C(43)-C(44)	1.363(3)	C(44)-C(45)	1.377(3)
C(45)-C(46)	1.379(3)		
C(1)-Ru(1)-C(2)	98.44(7)	C(1)-Ru(1)-C(6)	174.86(8)
C(2)-Ru(1)-C(6)	76.88(7)	C(1)-Ru(1)-P(1)	88.25(5)
C(2)-Ru(1)-P(1)	99.83(5)	C(6)-Ru(1)-P(1)	90.44(5)
C(1)-Ru(1)-P(2)	95.41(6)	C(2)-Ru(1)-P(2)	94.25(5)
C(6)-Ru(1)-P(2)	87.14(5)	P(1)-Ru(1)-P(2)	164.789(17)
C(29)-P(1)-C(41)	97.85(8)	C(29)-P(1)-C(35)	102.45(8)
C(41)-P(1)-C(35)	102.49(8)	C(29)-P(1)-Ru(1)	116.16(6)
C(41)-P(1)-Ru(1)	117.09(6)	C(35)-P(1)-Ru(1)	117.80(6)
C(17)-P(2)-C(11)	102.40(8)	C(17)-P(2)-C(23)	101.06(8)
C(11)-P(2)-C(23)	102.37(8)	C(17)-P(2)-Ru(1)	116.79(6)
C(11)-P(2)-Ru(1)	114.95(6)	C(23)-P(2)-Ru(1)	116.96(6)
C(2)-N(2)-C(4)	111.49(15)	C(2)-N(2)-C(7)	124.28(16)
C(4)-N(2)-C(7)	124.23(16)	C(2)-N(1)-C(3)	112.16(16)
C(2)-N(1)-C(5)	118.68(15)	C(3)-N(1)-C(5)	129.12(16)
O(1)-C(1)-Ru(1)	176.38(17)	N(2)-C(2)-N(1)	103.60(15)
N(2)-C(2)-Ru(1)	138.54(13)	N(1)-C(2)-Ru(1)	117.82(12)
C(4)-C(3)-N(1)	106.25(16)	C(4)-C(3)-C(9)	130.82(19)

N(1)-C(3)-C(9)	122.90(19)	C(3)-C(4)-N(2)	106.49(17)
C(3)-C(4)-C(10)	131.13(19)	N(2)-C(4)-C(10)	122.33(19)
N(1)-C(5)-C(6)	108.78(14)	C(5)-C(6)-Ru(1)	109.95(11)
N(2)-C(7)-C(8)	112.09(18)	C(16)-C(11)-C(12)	118.24(17)
C(16)-C(11)-P(2)	123.73(14)	C(12)-C(11)-P(2)	117.73(13)
C(13)-C(12)-C(11)	121.51(18)	C(12)-C(13)-C(14)	119.41(19)
C(15)-C(14)-C(13)	119.86(19)	C(14)-C(15)-C(16)	120.6(2)
C(15)-C(16)-C(11)	120.21(19)	C(18)-C(17)-C(22)	118.47(17)
C(18)-C(17)-P(2)	122.83(14)	C(22)-C(17)-P(2)	118.60(14)
C(17)-C(18)-C(19)	120.20(18)	C(20)-C(19)-C(18)	120.74(19)
C(19)-C(20)-C(21)	119.34(18)	C(20)-C(21)-C(22)	120.42(19)
C(21)-C(22)-C(17)	120.78(18)	C(28)-C(23)-C(24)	117.95(17)
C(28)-C(23)-P(2)	122.79(15)	C(24)-C(23)-P(2)	119.26(14)
C(25)-C(24)-C(23)	121.2(2)	C(26)-C(25)-C(24)	120.0(2)
C(27)-C(26)-C(25)	119.9(2)	C(26)-C(27)-C(28)	120.4(2)
C(23)-C(28)-C(27)	120.5(2)	C(34)-C(29)-C(30)	118.05(17)
C(34)-C(29)-P(1)	121.75(13)	C(30)-C(29)-P(1)	120.19(14)
C(31)-C(30)-C(29)	120.56(19)	C(32)-C(31)-C(30)	120.44(19)
C(33)-C(32)-C(31)	119.70(18)	C(32)-C(33)-C(34)	120.15(19)
C(29)-C(34)-C(33)	121.08(18)	C(40)-C(35)-C(36)	117.83(17)
C(40)-C(35)-P(1)	123.80(15)	C(36)-C(35)-P(1)	118.31(14)
C(37)-C(36)-C(35)	121.25(18)	C(38)-C(37)-C(36)	120.1(2)
C(39)-C(38)-C(37)	119.65(19)	C(38)-C(39)-C(40)	120.4(2)
C(39)-C(40)-C(35)	120.8(2)	C(42)-C(41)-C(46)	118.25(17)
C(42)-C(41)-P(1)	125.04(15)	C(46)-C(41)-P(1)	116.70(14)
C(41)-C(42)-C(43)	120.2(2)	C(44)-C(43)-C(42)	120.5(2)
C(43)-C(44)-C(45)	119.97(19)	C(44)-C(45)-C(46)	119.7(2)
C(45)-C(46)-C(41)	121.3(2)		

Table S-9. Anisotropic displacement parameters ($Å^2$ x 10^3) for [Ru(IEt_2Me_2)′(PPh_3)$_2$(CO)H] **3**. The anisotropic displacement factor exponent takes the form: -2 gpi^2 [h^2 a^{*2} U11 + ... + 2 h k a* b* U

Atom	U11	U22	U33	U23	U13	U12
Ru(1)	21(1)	24(1)	23(1)	2(1)	7(1)	2(1)
P(1)	23(1)	29(1)	23(1)	3(1)	7(1)	2(1)
P(2)	24(1)	26(1)	21(1)	2(1)	7(1)	2(1)
O(1)	35(1)	49(1)	53(1)	8(1)	24(1)	8(1)
N(2)	28(1)	27(1)	38(1)	2(1)	10(1)	1(1)
N(1)	25(1)	31(1)	31(1)	-3(1)	8(1)	5(1)
C(1)	29(1)	30(1)	28(1)	4(1)	8(1)	6(1)
C(2)	22(1)	29(1)	26(1)	1(1)	6(1)	2(1)
C(3)	29(1)	32(1)	42(1)	-7(1)	6(1)	5(1)
C(4)	30(1)	27(1)	50(1)	-2(1)	8(1)	3(1)
C(5)	29(1)	45(1)	31(1)	0(1)	13(1)	5(1)
C(6)	26(1)	35(1)	27(1)	6(1)	9(1)	1(1)
C(7)	41(1)	34(1)	48(1)	6(1)	21(1)	0(1)
C(8)	38(1)	53(1)	80(2)	-6(1)	30(1)	-9(1)
C(9)	44(1)	44(1)	56(1)	-12(1)	17(1)	10(1)
C(10)	52(1)	27(1)	91(2)	2(1)	25(1)	2(1)
C(11)	22(1)	29(1)	26(1)	4(1)	6(1)	1(1)
C(12)	29(1)	36(1)	26(1)	2(1)	7(1)	4(1)
C(13)	35(1)	38(1)	43(1)	-1(1)	8(1)	10(1)
C(14)	45(1)	39(1)	69(2)	24(1)	19(1)	14(1)
C(15)	49(1)	61(2)	61(2)	38(1)	32(1)	22(1)
C(16)	36(1)	47(1)	39(1)	16(1)	19(1)	15(1)
C(17)	29(1)	30(1)	25(1)	-2(1)	8(1)	-2(1)
C(18)	32(1)	40(1)	29(1)	5(1)	5(1)	-3(1)
C(19)	29(1)	56(1)	36(1)	3(1)	3(1)	-9(1)
C(20)	42(1)	49(1)	37(1)	-5(1)	11(1)	-19(1)
C(21)	50(1)	35(1)	41(1)	5(1)	10(1)	-11(1)
C(22)	36(1)	32(1)	40(1)	5(1)	7(1)	-3(1)
C(23)	32(1)	35(1)	22(1)	1(1)	7(1)	8(1)
C(24)	37(1)	40(1)	31(1)	4(1)	14(1)	10(1)
C(25)	42(1)	57(1)	36(1)	8(1)	19(1)	17(1)
C(26)	54(1)	62(2)	33(1)	-4(1)	16(1)	23(1)
C(27)	55(1)	53(1)	41(1)	-16(1)	10(1)	9(1)
C(28)	41(1)	44(1)	37(1)	-8(1)	11(1)	3(1)
C(29)	25(1)	31(1)	32(1)	7(1)	8(1)	3(1)
C(30)	38(1)	54(1)	32(1)	9(1)	13(1)	15(1)
C(31)	42(1)	63(2)	43(1)	23(1)	16(1)	24(1)
C(32)	37(1)	40(1)	53(1)	13(1)	19(1)	13(1)
C(33)	38(1)	33(1)	43(1)	2(1)	14(1)	5(1)
C(34)	34(1)	30(1)	33(1)	3(1)	8(1)	4(1)
C(35)	30(1)	36(1)	22(1)	2(1)	9(1)	-5(1)
C(36)	34(1)	37(1)	30(1)	0(1)	5(1)	-2(1)
C(37)	48(1)	37(1)	34(1)	0(1)	8(1)	-7(1)
C(38)	46(1)	51(1)	31(1)	-3(1)	9(1)	-21(1)

C(39)	30(1)	62(1)	40(1)	0(1)	10(1)	-10(1)
C(40)	31(1)	46(1)	35(1)	0(1)	12(1)	-2(1)
C(41)	27(1)	34(1)	28(1)	8(1)	9(1)	6(1)
C(42)	45(1)	41(1)	35(1)	0(1)	16(1)	-2(1)
C(43)	60(1)	60(1)	36(1)	0(1)	25(1)	3(1)
C(44)	48(1)	57(1)	47(1)	19(1)	26(1)	4(1)
C(45)	42(1)	42(1)	54(1)	14(1)	21(1)	2(1)
C(46)	37(1)	37(1)	40(1)	6(1)	14(1)	1(1)

Table S-10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for [Ru(IEt$_2$Me$_2$)′(PPh$_3$)$_2$(CO)H] **3**.

Atom	x	y	z	U(eq)
H(7A)	2838	4137	6606	48
H(7B)	2930	2632	6662	48
H(8A)	4002	4334	7536	81
H(8B)	4260	3642	7012	81
H(8C)	4111	2830	7549	81
H(9A)	1249	5708	8063	72
H(9B)	1378	4592	8553	72
H(9C)	593	4566	7929	72
H(10A)	2000	5896	6837	85
H(10B)	2905	5904	7357	85
H(10C)	2109	6412	7510	85
H(12)	431	2135	6804	37
H(13)	-2	4178	6481	48
H(14)	231	4997	5613	61
H(15)	783	3706	5032	64
H(16)	1205	1647	5349	47
H(18)	-451	285	5793	41
H(19)	-1584	-1026	5731	51
H(20)	-1384	-2885	6301	52
H(21)	-45	-3424	6947	52
H(22)	1076	-2069	7058	45
H(24)	2641	697	5959	42
H(25)	3075	-163	5193	52
H(26)	2399	-1935	4649	59
H(27)	1290	-2837	4871	61
H(28)	830	-1965	5631	49
H(30)	4354	-1477	9458	49
H(31)	5199	-3264	9578	59
H(32)	5373	-4235	8727	51
H(33)	4675	-3448	7750	45
H(34)	3795	-1698	7620	40
H(36)	3188	2655	8627	42
H(37)	4096	4321	9043	49
H(38)	5535	3961	9462	52
H(39)	6058	1926	9469	53
H(40)	5154	247	9055	44
H(42)	3251	1124	9604	47
H(43)	2603	506	10308	60
H(44)	1863	-1367	10173	58
H(45)	1726	-2627	9320	53
H(46)	2341	-2004	8609	45
H(1)	2386	-1144	7451	12(4)
H(6A)	784	455	7489	24(5)
H(6B)	1319	-39	8119	31(5)
H(5A)	860(8)	2172(18)	8106(9)	37(5)

H(5B)	1701(11)	1850(20)	8532(5)	41(6)