SUPPORTING INFORMATION

X-ray Reports for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (2)

and TpRu(CO)(*N*-pyrrolyl)(NCMe) (3)

Ruthenium(II)-Mediated Carbon-Carbon Bond Formation between Acetonitrile and Pyrrole: Combined Experimental and Computational Study

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TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (2)

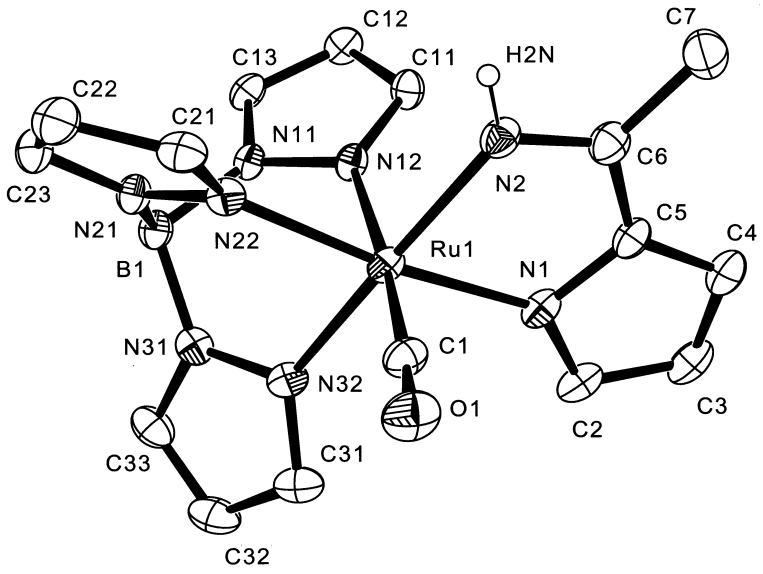

Figure 1. ORTEP (30 % probability) of TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**).

Experimental. A pink irregularly-shaped crystal of TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**), approximate dimensions 0.30 mm x 0.16 mm x 0.10 mm, was used for the X-ray crystallographic analysis. A full hemisphere of intensity data (1868 10-second frames with an ω scan width of 0.3º) was measured at 193(2) K on a Bruker SMART APEX CCD area detector system equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube (λ = 0.71073 Å) operated at 1.5 kW power (50 kV, 30 mA). The detector was placed at a distance of 6.00 cm. from the crystal.

The frames were integrated with the Bruker SAINT software package using a narrow-frame integration algorithm. The integration of the data using a monoclinic unit cell yielded a total of 19243 reflections to a maximum 2θ angle of 61.04° of which 5501 were independent (average redundancy 4.16, completeness = 96.8%, R_{int} = 0.043) and 4297 (78.1 %) were greater

than $2\sigma(I)$. The final cell constants of a = 7.8719(6) Å, b = 17.595(1) Å, c = 13.497(1) Å, β = 96.007(1)°, volume = 1859.1(3) Å^3, are based upon the refinement of the XYZ-centroids of 5777 reflections with $7.58° < 2\theta < 56.02°$. Analysis of the data showed negligible decay during data collection. Data were corrected for absorption effects using empirical techniques, with minimum and maximum transmission coefficients of 0.463 and 0.523, respectively.

The structure was solved and refined using the Bruker SHELXTL (Version 6.1) Software Package, using the space group $P2_1/c$, with Z = 4 for the formula unit, Ru[HB(N2C3H3)3]-(CO)(NHC(CH3)(NC4H3)). The final anisotropic full-matrix least-squares refinement on F^2 with 253 variables converged at R1 = 4.04%, for the 4297 observed data and wR2 = 8.92% for all data. The goodness-of-fit was 0.963. Hydrogen atoms H_1 and H_{2N} were located from a difference Fourier map and refined as independent isotropic atoms. The methyl group (C_7 and its hydrogens) was refined as a rigid rotor with idealized sp^3-hybridized geometry and a C-H bond length of 0.98 Å. The remaining hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2-hybridization of the carbon atoms and C-H bond lengths of 0.95 Å) "riding" on their respective carbon atoms. The isotropic thermal parameter for H_1 and H_{2N} refined to final U_{iso} values of 0.033(7) Å^2 and 0.042(8) Å^2, respectively. The isotropic thermal parameters of the remaining hydrogen atoms were fixed at values 1.2 (non-methyl) or 1.5 (methyl) times the equivalent isotropic thermal parameters of the carbon atoms to which they are covalently bonded.

The largest peak on the final difference map was 1.43 e^-/Å^3 and the largest hole was -0.45 e^-/Å^3. The top six peaks in the final difference Fourier map (1.43 – 0.67 e^-/Å^3) were within 0.90 Å of the Ru atom. On the basis of the final model, the calculated density was 1.605 g/cm^3 and F(000), 904 e^-.

Table 1. Crystal data and structure refinement for $TpRu(CO)\{\kappa^2\text{-}N,N\text{-}(H)N{=}C(Me)\text{-}(NC_4H_3)\}$ (**2**).

Empirical formula	C16 H17 B N8 O Ru
Formula weight	449.26
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 7.8719(6) Å
	b = 17.5946(14) Å, β = 96.007(1)°
	c = 13.4970(11) Å
Volume	1859.1(3) $Å^3$
Z	4
Density (calculated)	1.605 Mg/m^3
Absorption coefficient	0.867 mm^{-1}
F(000)	904
Crystal size	0.30 x 0.16 x 0.10 mm^3
Theta range for data collection	3.79 to 30.52°.
Index ranges	$-11\leq h\leq 11$, $-24\leq k\leq 24$, $-18\leq l\leq 18$
Reflections collected	19243
Independent reflections	5501 [R(int) = 0.0427]
Completeness to theta = 30.52°	96.8 %
Absorption correction	Empirical
Max. and min. transmission	0.5230 and 0.4627
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5501 / 0 / 253
Goodness-of-fit on F^2	0.963
Final R indices [I>2sigma(I)]	R1 = 0.0404, wR2 = 0.0842
R indices (all data)	R1 = 0.0559, wR2 = 0.0892
Largest diff. peak and hole	1.432 and -0.447 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**).
U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	4223(1)	4234(1)	2295(1)	29(1)
N(11)	3019(2)	5845(1)	1778(2)	29(1)
N(12)	2896(2)	5112(1)	1437(2)	30(1)
C(11)	2026(3)	5145(2)	532(2)	35(1)
C(12)	1588(3)	5889(1)	284(2)	37(1)
C(13)	2236(3)	6310(1)	1088(2)	35(1)
N(21)	5966(2)	5738(1)	2633(2)	32(1)
N(22)	6236(2)	5001(1)	2379(2)	30(1)
C(21)	7904(3)	4941(2)	2282(2)	38(1)
C(22)	8713(4)	5627(2)	2473(2)	48(1)
C(23)	7445(3)	6119(2)	2688(2)	42(1)
N(31)	3458(3)	5543(1)	3595(2)	35(1)
N(32)	3421(3)	4772(1)	3542(2)	34(1)
C(31)	2798(4)	4528(2)	4364(2)	44(1)
C(32)	2416(4)	5137(2)	4953(2)	51(1)
C(33)	2842(4)	5769(2)	4442(2)	45(1)
B(1)	4138(4)	6013(2)	2762(2)	34(1)
O(1)	6511(3)	3144(1)	3479(2)	52(1)
C(1)	5558(3)	3543(2)	3033(2)	36(1)
N(1)	2150(3)	3509(1)	2019(2)	35(1)
N(2)	4674(3)	3728(1)	963(2)	36(1)
C(2)	732(3)	3305(2)	2431(2)	42(1)
C(3)	-199(3)	2776(2)	1820(2)	47(1)
C(4)	680(3)	2648(2)	1007(2)	43(1)
C(5)	2142(3)	3108(1)	1142(2)	36(1)
C(6)	3556(3)	3243(2)	575(2)	39(1)
C(7)	3695(4)	2845(2)	-384(2)	57(1)

Table 3. Bond lengths [Å] and angles [°] for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**).

Ru(1)-C(1)	1.831(3)
Ru(1)-N(2)	2.070(2)
Ru(1)-N(1)	2.073(2)
Ru(1)-N(22)	2.076(2)
Ru(1)-N(32)	2.085(2)
Ru(1)-N(12)	2.1373(19)
N(11)-C(13)	1.341(3)
N(11)-N(12)	1.369(2)
N(11)-B(1)	1.543(4)
N(12)-C(11)	1.337(3)
C(11)-C(12)	1.385(3)
C(12)-C(13)	1.368(4)
N(21)-C(23)	1.339(3)
N(21)-N(22)	1.363(3)
N(21)-B(1)	1.545(3)
N(22)-C(21)	1.337(3)
C(21)-C(22)	1.376(4)
C(22)-C(23)	1.375(4)
N(31)-C(33)	1.347(3)
N(31)-N(32)	1.358(3)
N(31)-B(1)	1.537(4)
N(32)-C(31)	1.330(3)
C(31)-C(32)	1.386(4)
C(32)-C(33)	1.368(4)
O(1)-C(1)	1.151(3)
N(1)-C(2)	1.348(3)
N(1)-C(5)	1.377(3)
N(2)-C(6)	1.297(3)
C(2)-C(3)	1.399(4)
C(3)-C(4)	1.375(4)
C(4)-C(5)	1.403(4)
C(5)-C(6)	1.435(4)
C(6)-C(7)	1.485(4)

C(1)-Ru(1)-N(2)	92.62(10)
C(1)-Ru(1)-N(1)	94.92(10)
N(2)-Ru(1)-N(1)	77.44(9)
C(1)-Ru(1)-N(22)	90.62(10)
N(2)-Ru(1)-N(22)	97.34(8)
N(1)-Ru(1)-N(22)	172.54(8)
C(1)-Ru(1)-N(32)	93.89(10)
N(2)-Ru(1)-N(32)	171.91(8)
N(1)-Ru(1)-N(32)	97.21(8)
N(22)-Ru(1)-N(32)	87.38(8)
C(1)-Ru(1)-N(12)	174.06(9)
N(2)-Ru(1)-N(12)	87.66(8)
N(1)-Ru(1)-N(12)	90.93(7)
N(22)-Ru(1)-N(12)	83.47(7)
N(32)-Ru(1)-N(12)	86.36(8)
C(13)-N(11)-N(12)	109.2(2)
C(13)-N(11)-B(1)	131.3(2)
N(12)-N(11)-B(1)	118.97(19)
C(11)-N(12)-N(11)	106.14(19)
C(11)-N(12)-Ru(1)	134.48(17)
N(11)-N(12)-Ru(1)	119.02(15)
N(12)-C(11)-C(12)	110.7(2)
C(13)-C(12)-C(11)	104.9(2)
N(11)-C(13)-C(12)	109.1(2)
C(23)-N(21)-N(22)	109.4(2)
C(23)-N(21)-B(1)	130.7(2)
N(22)-N(21)-B(1)	119.86(19)
C(21)-N(22)-N(21)	106.3(2)
C(21)-N(22)-Ru(1)	134.03(18)
N(21)-N(22)-Ru(1)	119.60(14)
N(22)-C(21)-C(22)	110.6(2)
C(23)-C(22)-C(21)	105.1(2)
N(21)-C(23)-C(22)	108.6(2)
C(33)-N(31)-N(32)	109.4(2)
C(33)-N(31)-B(1)	130.2(2)
N(32)-N(31)-B(1)	120.4(2)

C(31)-N(32)-N(31)	106.6(2)
C(31)-N(32)-Ru(1)	134.1(2)
N(31)-N(32)-Ru(1)	119.34(16)
N(32)-C(31)-C(32)	110.5(3)
C(33)-C(32)-C(31)	105.0(3)
N(31)-C(33)-C(32)	108.5(3)
N(31)-B(1)-N(11)	108.4(2)
N(31)-B(1)-N(21)	108.3(2)
N(11)-B(1)-N(21)	107.3(2)
O(1)-C(1)-Ru(1)	174.3(2)
C(2)-N(1)-C(5)	106.8(2)
C(2)-N(1)-Ru(1)	139.4(2)
C(5)-N(1)-Ru(1)	113.77(16)
C(6)-N(2)-Ru(1)	117.58(18)
N(1)-C(2)-C(3)	109.8(3)
C(4)-C(3)-C(2)	107.7(2)
C(3)-C(4)-C(5)	106.0(3)
N(1)-C(5)-C(4)	109.8(2)
N(1)-C(5)-C(6)	116.0(2)
C(4)-C(5)-C(6)	134.2(3)
N(2)-C(6)-C(5)	115.2(2)
N(2)-C(6)-C(7)	123.6(3)
C(5)-C(6)-C(7)	121.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**). The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	26(1)	26(1)	36(1)	3(1)	6(1)	2(1)
N(11)	26(1)	24(1)	38(1)	-1(1)	2(1)	0(1)
N(12)	25(1)	25(1)	38(1)	1(1)	0(1)	-1(1)
C(11)	27(1)	35(1)	41(1)	-3(1)	-4(1)	-3(1)
C(12)	31(1)	37(1)	42(2)	8(1)	-2(1)	2(1)
C(13)	29(1)	28(1)	47(2)	7(1)	5(1)	1(1)
N(21)	26(1)	32(1)	38(1)	-2(1)	1(1)	-4(1)
N(22)	25(1)	33(1)	33(1)	1(1)	3(1)	2(1)
C(21)	27(1)	51(2)	36(1)	3(1)	7(1)	6(1)
C(22)	26(1)	67(2)	50(2)	1(1)	4(1)	-10(1)
C(23)	34(1)	46(2)	45(2)	-2(1)	-2(1)	-12(1)
N(31)	30(1)	38(1)	36(1)	-4(1)	4(1)	4(1)
N(32)	30(1)	36(1)	37(1)	5(1)	7(1)	3(1)
C(31)	39(2)	56(2)	39(2)	11(1)	8(1)	5(1)
C(32)	42(2)	76(2)	35(2)	3(2)	11(1)	8(2)
C(33)	39(2)	57(2)	38(2)	-11(1)	4(1)	8(1)
B(1)	31(1)	28(1)	41(2)	-3(1)	2(1)	1(1)
O(1)	56(1)	41(1)	58(1)	12(1)	5(1)	17(1)
C(1)	39(1)	29(1)	41(1)	4(1)	11(1)	4(1)
N(1)	30(1)	27(1)	49(1)	7(1)	9(1)	1(1)
N(2)	34(1)	30(1)	45(1)	0(1)	13(1)	-1(1)
C(2)	34(1)	35(2)	58(2)	14(1)	14(1)	4(1)
C(3)	32(1)	38(2)	72(2)	17(1)	6(1)	-3(1)
C(4)	38(1)	30(1)	60(2)	7(1)	-1(1)	-1(1)
C(5)	36(1)	24(1)	48(2)	6(1)	5(1)	1(1)
C(6)	39(2)	31(1)	48(2)	1(1)	8(1)	3(1)
C(7)	61(2)	54(2)	57(2)	-14(2)	16(2)	-12(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**).

	x	y	z	U(eq)
H(11)	1747	4718	117	42
H(12)	971	6067	-314	45
H(13)	2147	6846	1147	42
H(21)	8454	4488	2106	45
H(22)	9892	5737	2459	57
H(23)	7594	6642	2848	50
H(31)	2637	4009	4524	53
H(32)	1957	5119	5576	61
H(33)	2725	6280	4650	53
H(1)	4150(30)	6620(14)	2977(19)	33(7)
H(2N)	5530(40)	3782(16)	610(20)	42(8)
H(2)	412	3492	3045	50
H(3)	-1250	2547	1943	57
H(4)	362	2315	465	52
H(7A)	4518	3112	-755	85
H(7B)	2576	2839	-777	85
H(7C)	4082	2322	-251	85

Table 6. Torsion angles [°] for TpRu(CO){κ^2-*N*,*N*-(H)N=C(Me)-(NC_4H_3)} (**2**).

C(13)-N(11)-N(12)-C(11)	-0.1(3)
B(1)-N(11)-N(12)-C(11)	-173.0(2)
C(13)-N(11)-N(12)-Ru(1)	174.03(15)
B(1)-N(11)-N(12)-Ru(1)	1.0(3)
C(1)-Ru(1)-N(12)-C(11)	121.2(9)
N(2)-Ru(1)-N(12)-C(11)	28.3(2)
N(1)-Ru(1)-N(12)-C(11)	-49.1(2)
N(22)-Ru(1)-N(12)-C(11)	126.0(2)
N(32)-Ru(1)-N(12)-C(11)	-146.3(2)
C(1)-Ru(1)-N(12)-N(11)	-50.9(10)
N(2)-Ru(1)-N(12)-N(11)	-143.74(17)
N(1)-Ru(1)-N(12)-N(11)	138.87(17)
N(22)-Ru(1)-N(12)-N(11)	-46.07(16)
N(32)-Ru(1)-N(12)-N(11)	41.70(16)
N(11)-N(12)-C(11)-C(12)	0.1(3)
Ru(1)-N(12)-C(11)-C(12)	-172.69(17)
N(12)-C(11)-C(12)-C(13)	0.0(3)
N(12)-N(11)-C(13)-C(12)	0.0(3)
B(1)-N(11)-C(13)-C(12)	171.9(2)
C(11)-C(12)-C(13)-N(11)	0.0(3)
C(23)-N(21)-N(22)-C(21)	0.1(3)
B(1)-N(21)-N(22)-C(21)	177.5(2)
C(23)-N(21)-N(22)-Ru(1)	177.06(17)
B(1)-N(21)-N(22)-Ru(1)	-5.6(3)
C(1)-Ru(1)-N(22)-C(21)	43.7(2)
N(2)-Ru(1)-N(22)-C(21)	-49.1(2)
N(1)-Ru(1)-N(22)-C(21)	-94.3(6)
N(32)-Ru(1)-N(22)-C(21)	137.5(2)
N(12)-Ru(1)-N(22)-C(21)	-135.8(2)
C(1)-Ru(1)-N(22)-N(21)	-132.26(18)
N(2)-Ru(1)-N(22)-N(21)	135.02(17)
N(1)-Ru(1)-N(22)-N(21)	89.8(6)
N(32)-Ru(1)-N(22)-N(21)	-38.39(17)
N(12)-Ru(1)-N(22)-N(21)	48.24(17)

N(21)-N(22)-C(21)-C(22)	0.2(3)
Ru(1)-N(22)-C(21)-C(22)	-176.13(19)
N(22)-C(21)-C(22)-C(23)	-0.4(3)
N(22)-N(21)-C(23)-C(22)	-0.4(3)
B(1)-N(21)-C(23)-C(22)	-177.3(3)
C(21)-C(22)-C(23)-N(21)	0.4(3)
C(33)-N(31)-N(32)-C(31)	-0.6(3)
B(1)-N(31)-N(32)-C(31)	179.2(2)
C(33)-N(31)-N(32)-Ru(1)	178.20(16)
B(1)-N(31)-N(32)-Ru(1)	-2.0(3)
C(1)-Ru(1)-N(32)-C(31)	-48.6(3)
N(2)-Ru(1)-N(32)-C(31)	94.9(6)
N(1)-Ru(1)-N(32)-C(31)	46.8(3)
N(22)-Ru(1)-N(32)-C(31)	-139.1(3)
N(12)-Ru(1)-N(32)-C(31)	137.3(3)
C(1)-Ru(1)-N(32)-N(31)	132.96(19)
N(2)-Ru(1)-N(32)-N(31)	-83.5(6)
N(1)-Ru(1)-N(32)-N(31)	-131.58(17)
N(22)-Ru(1)-N(32)-N(31)	42.52(17)
N(12)-Ru(1)-N(32)-N(31)	-41.10(17)
N(31)-N(32)-C(31)-C(32)	0.4(3)
Ru(1)-N(32)-C(31)-C(32)	-178.20(19)
N(32)-C(31)-C(32)-C(33)	0.0(3)
N(32)-N(31)-C(33)-C(32)	0.6(3)
B(1)-N(31)-C(33)-C(32)	-179.2(2)
C(31)-C(32)-C(33)-N(31)	-0.4(3)
C(33)-N(31)-B(1)-N(11)	-119.8(3)
N(32)-N(31)-B(1)-N(11)	60.4(3)
C(33)-N(31)-B(1)-N(21)	124.2(3)
N(32)-N(31)-B(1)-N(21)	-55.6(3)
C(13)-N(11)-B(1)-N(31)	130.1(3)
N(12)-N(11)-B(1)-N(31)	-58.7(3)
C(13)-N(11)-B(1)-N(21)	-113.2(3)
N(12)-N(11)-B(1)-N(21)	58.0(3)
C(23)-N(21)-B(1)-N(31)	-123.0(3)
N(22)-N(21)-B(1)-N(31)	60.3(3)

C(23)-N(21)-B(1)-N(11)	120.2(3)
N(22)-N(21)-B(1)-N(11)	-56.5(3)
N(2)-Ru(1)-C(1)-O(1)	82(2)
N(1)-Ru(1)-C(1)-O(1)	159(2)
N(22)-Ru(1)-C(1)-O(1)	-16(2)
N(32)-Ru(1)-C(1)-O(1)	-103(2)
N(12)-Ru(1)-C(1)-O(1)	-11(3)
C(1)-Ru(1)-N(1)-C(2)	88.8(3)
N(2)-Ru(1)-N(1)-C(2)	-179.6(3)
N(22)-Ru(1)-N(1)-C(2)	-133.5(6)
N(32)-Ru(1)-N(1)-C(2)	-5.8(3)
N(12)-Ru(1)-N(1)-C(2)	-92.2(3)
C(1)-Ru(1)-N(1)-C(5)	-92.71(18)
N(2)-Ru(1)-N(1)-C(5)	-1.11(16)
N(22)-Ru(1)-N(1)-C(5)	45.0(7)
N(32)-Ru(1)-N(1)-C(5)	172.73(16)
N(12)-Ru(1)-N(1)-C(5)	86.28(17)
C(1)-Ru(1)-N(2)-C(6)	95.7(2)
N(1)-Ru(1)-N(2)-C(6)	1.28(19)
N(22)-Ru(1)-N(2)-C(6)	-173.30(19)
N(32)-Ru(1)-N(2)-C(6)	-47.9(7)
N(12)-Ru(1)-N(2)-C(6)	-90.2(2)
C(5)-N(1)-C(2)-C(3)	-0.4(3)
Ru(1)-N(1)-C(2)-C(3)	178.17(19)
N(1)-C(2)-C(3)-C(4)	0.3(3)
C(2)-C(3)-C(4)-C(5)	-0.1(3)
C(2)-N(1)-C(5)-C(4)	0.3(3)
Ru(1)-N(1)-C(5)-C(4)	-178.68(16)
C(2)-N(1)-C(5)-C(6)	179.9(2)
Ru(1)-N(1)-C(5)-C(6)	0.9(3)
C(3)-C(4)-C(5)-N(1)	-0.1(3)
C(3)-C(4)-C(5)-C(6)	-179.5(3)
Ru(1)-N(2)-C(6)-C(5)	-1.2(3)
Ru(1)-N(2)-C(6)-C(7)	179.0(2)
N(1)-C(5)-C(6)-N(2)	0.2(3)
C(4)-C(5)-C(6)-N(2)	179.6(3)

N(1)-C(5)-C(6)-C(7)	-180.0(3)
C(4)-C(5)-C(6)-C(7)	-0.5(5)

Symmetry transformations used to generate equivalent atoms:

TpRu(CO)(*N*-pyrrolyl)(NCMe) (3)

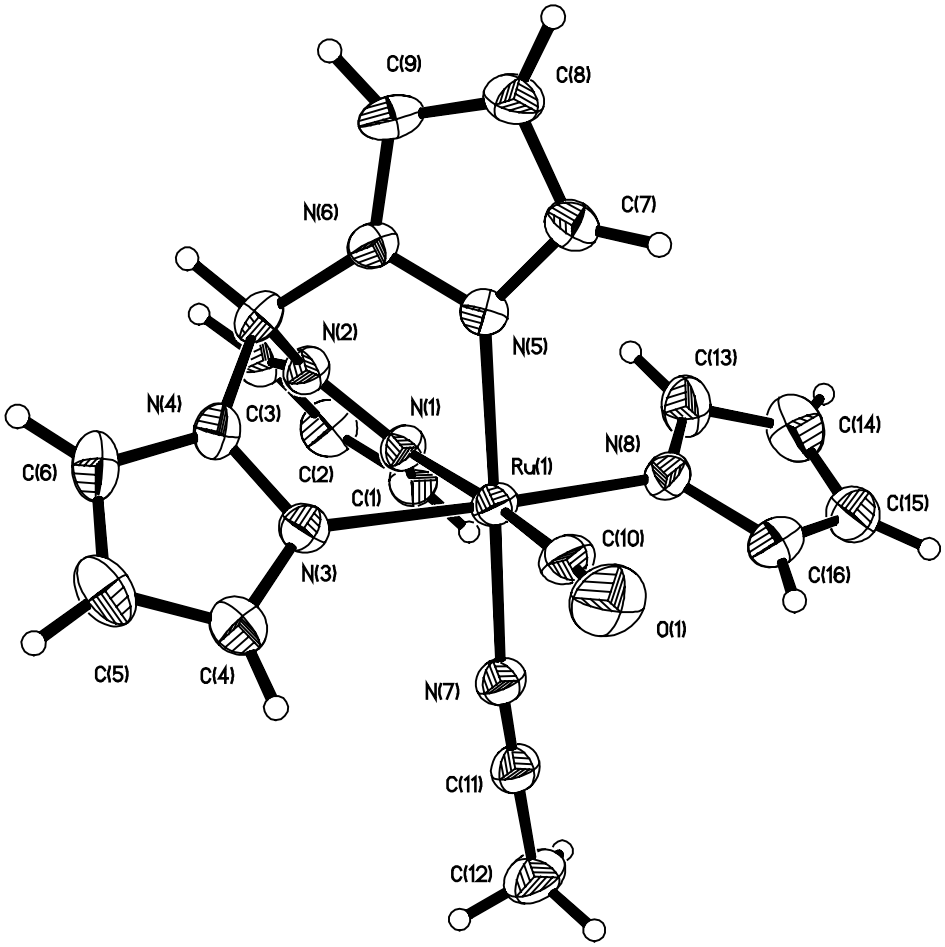

Figure 2. Perspective view of the molecular structure of TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**) with the atom numbering scheme. The thermal ellipsoids are scaled to enclose 30% probability.

Experimental. A light yellow irregular crystalline fragment was washed with the perfluoropolyether PFO-XR75 (Lancaster) and sealed under nitrogen in a glass capillary. The crystal was optically aligned on the four-circle of a Siemens P4 diffractometer equipped with a graphite monochromator, a Mo Kα radiation source (λ = 0.71073 Å), and a SMART CCD detector held at 5.084 cm from the crystal. Four sets of 20 frames each were collected using the ω scan method with a 10 s exposure time. Integration of these frames followed by reflection indexing and least-squares refinement produced a crystal orientation matrix for the monoclinic crystal lattice.

Data collection consisted of the measurement of a total of 1650 frames in five different runs covering a hemisphere of data. Frame scan parameters are summarized below:

Run	2θ	ω	ϕ	χ	Scan axis	Scan width (°)	Frames (#)	Exposure time (sec.)
1	28	43.00	0.00	280.00	2	-0.3	100	40
2	28	43.00	90.00	280.00	2	-0.3	100	40
3	28	43.00	180.00	280.00	2	-0.3	100	40
4	28	43.00	270.00	280.00	2	-0.3	100	40
5	28	28.00	0.00	30.00	3	0.3	1250	40

The program SMART (version 5.6)[1] was used for diffractometer control, frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, and the data collection. All 1650 crystallographic raw data frames were read by program SAINT (version 5/6.0)[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce a total of 15524 reflections and their intensities and estimated standard deviations. An

absorption correction was applied using the SADABS routine available in SAINT.[1] The data were corrected for Lorentz and polarization effects as well as any crystal decay. Data preparation was carried out by using the program XPREP,[1] which gave 4295 unique reflections (R_{int} = 7.39 %) with indices $-13 \leq h \leq 13$, $-14 \leq k \leq 15$, $-20 \leq l \leq 20$. The monoclinic space group was determined to be $P2_1/n$, a non-standard setting for $P2_1/c$ (No. 14).

The structure was solved by a combination of direct methods and difference Fourier methods with the use of SHELXTL 6.1.[2] Idealized positions for all of the hydrogen atoms, with exception of the hydrogen atom bound to the boron atom, were included as fixed contributions using a riding model with isotropic temperature factors set at 1.2 (aromatic protons) or 1.5 (methyl protons) times that of the adjacent carbon atom. The positions of the methyl hydrogen atoms were optimized by a rigid rotating group refinement with idealized tetrahedral angles. The hydrogen atom on the boron atom was located and its position was refined. Full-matrix least-squares refinement, based upon the minimization of $\Sigma w_i |F_o^2 - F_c^2|^2$, with weighting $w_i^{-1} = [\sigma^2(F_o^2) + (0.0496\ P)^2 + 0.8866\ P]$, where $P = (\text{Max}(F_o^2, 0) + 2\ F_c^2)/3$, converged to give final discrepancy indices of R1 = 0.0478, wR2 = 0.0998 for 2644 with $I > 2\ \sigma(I)$.[3] The goodness of fit (GOF) value was 1.022.

A correction for secondary extinction was not applied. The maximum and minimum residual electron density peaks in the final difference Fourier map were 0.771 and -0.377 e/Å^3, respectively. The linear absorption coefficient, atomic scattering factors, and anomalous dispersion corrections were calculated from values found in the International Tables of X-ray Crystallography.[4]

References

1. SMART, SAINT and XPREP programs are part of Bruker crystallographic software package for single crystal data collection, reduction and preparation.
2. Sheldrick, G. M., SHELXTL6.1 (2000), Crystallographic software package, Bruker AXS, Inc. Madison, Wisconsin, USA.
3. $R_1 = \sum(||F_o| - |F_c||) / \sum|F_o|$, $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$, $R_{int.} = \sum|F_o^2 - F_o^2(mean)|^2 / \sum[F_o^2]$, and $GOF = [\sum[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$, where n is the number of reflections and p is the total number of parameters which were varied during the last refinement cycle.
4. International Tables for X-ray Crystallography (1974). Vol. IV, p. 55. Birmingham: Kynoch Press. (Present distributor, D. Reidel, Dordrecht.).

Table 7. Crystal data and structure refinement for TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**).

Empirical formula	$C_{16}H_{17}BN_8ORu$
Formula weight	449.26
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 10.413(2) Å α = 90° b = 12.170(2) Å β = 106.195(3)° c = 15.495(3) Å γ = 90°
Volume, Z	1885.7(6) Å^3, 4
Density (calculated)	1.582 g/cm^3
Absorption coefficient	8.55 cm^{-1}
F(000)	904
Crystal size	0.07 x 0.16 x 0.34 mm
θ range for data collection	2.11 to 27.52°
Limiting indices	$-13 \le h \le 13$ $-14 \le k \le 15$ $-20 \le l \le 20$
Reflections collected	15524 (98.9% completeness)
Independent reflections	4295 (R_{int} = 0.0739)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4295 / 0 / 248
Goodness-of-fit on F^2	1.022
Final R indices [I>2σ(I)]	R1 = 0.0478, wR2 = 0.0998
R indices (all data)	R1 = 0.1018, wR2 = 0.1170
Largest diff. peak and hole	0.771 and -0.377 eÅ^{-3}

Table 8. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**). U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Ru(1)	7623(1)	1872(1)	1104(1)	41(1)
O(1)	6313(5)	-317(4)	731(3)	84(1)
N(1)	8778(4)	3350(3)	1381(2)	43(1)
N(2)	9683(4)	3547(3)	915(2)	45(1)
N(3)	9450(4)	1137(3)	1128(2)	45(1)
N(4)	10231(4)	1615(3)	668(3)	48(1)
N(5)	7379(4)	2210(3)	-231(2)	42(1)
N(6)	8443(4)	2591(3)	-495(2)	44(1)
N(7)	7920(4)	1695(3)	2453(2)	49(1)
N(8)	5898(4)	2740(4)	1101(2)	48(1)
C(1)	8933(5)	4138(4)	1995(3)	53(1)
C(2)	9932(6)	4856(4)	1932(4)	64(2)
C(3)	10384(6)	4449(4)	1241(3)	59(1)
C(4)	10087(6)	239(4)	1515(3)	58(1)
C(5)	11271(7)	127(5)	1308(4)	71(2)
C(6)	11349(6)	1010(5)	776(4)	62(2)
C(7)	6322(5)	2186(4)	-959(3)	49(1)
C(8)	6711(6)	2553(5)	-1696(3)	58(1)
C(9)	8015(6)	2795(4)	-1385(3)	56(2)
C(10)	6767(5)	540(5)	862(3)	52(1)
C(11)	7974(5)	1712(4)	3189(3)	52(1)
C(12)	8029(7)	1744(5)	4136(3)	77(2)
C(13)	5685(6)	3839(5)	974(4)	66(2)
C(14)	4559(7)	4166(6)	1188(4)	77(2)
C(15)	4029(7)	3229(7)	1454(4)	80(2)
C(16)	4844(6)	2381(6)	1377(4)	74(2)
B(1)	9826(7)	2718(5)	199(4)	50(2)

Table 9. Interatomic distances [Å] and bond angles [°] for TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**).

Ru(1)-C(10)	1.836(6)
Ru(1)-N(7)	2.038(4)
Ru(1)-N(5)	2.054(3)
Ru(1)-N(8)	2.083(4)
Ru(1)-N(3)	2.094(4)
Ru(1)-N(1)	2.140(4)
O(1)-C(10)	1.140(6)
N(1)-C(1)	1.328(5)
N(1)-N(2)	1.359(5)
N(2)-C(3)	1.338(6)
N(2)-B(1)	1.537(7)
N(3)-C(4)	1.330(6)
N(3)-N(4)	1.353(5)
N(4)-C(6)	1.349(6)
N(4)-B(1)	1.528(7)
N(5)-C(7)	1.339(5)
N(5)-N(6)	1.365(5)
N(6)-C(9)	1.350(5)
N(6)-B(1)	1.546(7)
N(7)-C(11)	1.127(6)
N(8)-C(16)	1.357(7)
N(8)-C(13)	1.361(7)
C(1)-C(2)	1.383(7)
C(2)-C(3)	1.375(7)
C(4)-C(5)	1.366(8)
C(5)-C(6)	1.371(8)
C(7)-C(8)	1.388(6)
C(8)-C(9)	1.341(7)
C(11)-C(12)	1.453(6)
C(13)-C(14)	1.364(8)
C(14)-C(15)	1.379(8)
C(15)-C(16)	1.362(8)

C(10)-Ru(1)-N(7)	92.43(17)
C(10)-Ru(1)-N(5)	93.14(17)
N(7)-Ru(1)-N(5)	174.31(15)
C(10)-Ru(1)-N(8)	94.5(2)
N(7)-Ru(1)-N(8)	86.58(15)
N(5)-Ru(1)-N(8)	91.82(15)
C(10)-Ru(1)-N(3)	90.8(2)
N(7)-Ru(1)-N(3)	93.40(15)
N(5)-Ru(1)-N(3)	87.69(15)
N(8)-Ru(1)-N(3)	174.72(16)
C(10)-Ru(1)-N(1)	174.9(2)
N(7)-Ru(1)-N(1)	88.10(14)
N(5)-Ru(1)-N(1)	86.45(14)
N(8)-Ru(1)-N(1)	90.57(15)

N(3)-Ru(1)-N(1)	84.15(14)
C(1)-N(1)-N(2)	106.9(4)
C(1)-N(1)-Ru(1)	134.4(3)
N(2)-N(1)-Ru(1)	118.4(3)
C(3)-N(2)-N(1)	109.2(4)
C(3)-N(2)-B(1)	131.3(5)
N(1)-N(2)-B(1)	119.3(4)
C(4)-N(3)-N(4)	107.1(4)
C(4)-N(3)-Ru(1)	134.0(4)
N(4)-N(3)-Ru(1)	118.9(3)
C(6)-N(4)-N(3)	108.9(4)
C(6)-N(4)-B(1)	130.7(5)
N(3)-N(4)-B(1)	120.1(4)
C(7)-N(5)-N(6)	107.5(4)
C(7)-N(5)-Ru(1)	133.2(3)
N(6)-N(5)-Ru(1)	119.2(3)
C(9)-N(6)-N(5)	107.8(4)
C(9)-N(6)-B(1)	132.1(4)
N(5)-N(6)-B(1)	120.2(4)
C(11)-N(7)-Ru(1)	170.9(4)
C(16)-N(8)-C(13)	104.4(5)
C(16)-N(8)-Ru(1)	127.5(4)
C(13)-N(8)-Ru(1)	127.2(4)
N(1)-C(1)-C(2)	110.4(5)
C(3)-C(2)-C(1)	104.8(5)
N(2)-C(3)-C(2)	108.7(5)
N(3)-C(4)-C(5)	110.2(5)
C(4)-C(5)-C(6)	105.7(5)
N(4)-C(6)-C(5)	108.0(5)
N(5)-C(7)-C(8)	109.0(5)
C(9)-C(8)-C(7)	105.9(4)
C(8)-C(9)-N(6)	109.8(4)
O(1)-C(10)-Ru(1)	175.7(5)
N(7)-C(11)-C(12)	179.3(6)
N(8)-C(13)-C(14)	111.6(6)
C(13)-C(14)-C(15)	105.9(6)
C(16)-C(15)-C(14)	106.9(6)
N(8)-C(16)-C(15)	111.2(6)
N(4)-B(1)-N(2)	107.6(4)
N(4)-B(1)-N(6)	108.8(4)
N(2)-B(1)-N(6)	107.9(5)

Table 10. Anisotropic displacement parameters [$Å^2$ x 10^3] for TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**). The anisotropic displacement factor exponent takes the form: $-2\pi^2[(ha^*)^2U_{11} + ... + 2hka^*b^*U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru(1)	43(1)	45(1)	36(1)	1(1)	13(1)	-4(1)
O(1)	91(4)	63(3)	94(3)	0(2)	21(2)	-28(3)
N(1)	43(2)	46(2)	41(2)	-4(2)	15(2)	-3(2)
N(2)	43(3)	45(2)	49(2)	-2(2)	13(2)	-9(2)
N(3)	45(3)	43(3)	45(2)	1(2)	10(2)	-2(2)
N(4)	43(3)	46(3)	56(2)	-5(2)	19(2)	0(2)
N(5)	42(2)	43(2)	41(2)	2(2)	11(2)	1(2)
N(6)	49(3)	45(2)	40(2)	1(2)	15(2)	-6(2)
N(7)	50(3)	54(3)	42(2)	0(2)	15(2)	-6(2)
N(8)	44(3)	60(3)	43(2)	0(2)	16(2)	-1(2)
C(1)	52(3)	57(3)	48(3)	-9(2)	14(2)	-1(3)
C(2)	72(4)	50(3)	69(3)	-15(3)	16(3)	-11(3)
C(3)	59(4)	57(4)	61(3)	-4(3)	16(3)	-16(3)
C(4)	57(4)	55(4)	58(3)	0(2)	11(3)	5(3)
C(5)	67(4)	55(4)	84(4)	-5(3)	8(3)	21(3)
C(6)	44(3)	71(4)	74(3)	-17(3)	20(3)	5(3)
C(7)	50(3)	50(3)	44(2)	0(2)	6(2)	0(2)
C(8)	61(4)	70(4)	39(2)	0(2)	6(2)	-3(3)
C(9)	79(4)	55(3)	38(2)	1(2)	23(3)	-10(3)
C(10)	54(4)	57(4)	47(2)	7(2)	16(2)	-10(3)
C(11)	47(3)	62(4)	46(3)	0(2)	11(2)	-11(3)
C(12)	82(5)	109(5)	45(3)	-2(3)	26(3)	-19(4)
C(13)	52(4)	54(4)	90(4)	3(3)	19(3)	2(3)
C(14)	73(5)	76(5)	78(4)	-24(3)	18(3)	13(4)
C(15)	62(4)	130(6)	58(3)	11(4)	30(3)	27(5)
C(16)	66(4)	93(5)	70(3)	26(3)	31(3)	5(4)
B(1)	49(4)	52(4)	55(3)	0(3)	25(3)	-9(3)

Table 11. Hydrogen atom coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for TpRu(CO)(*N*-pyrrolyl)(NCMe) (**3**).

	x	y	z	U(eq)
H(1)	8440	4198	2409	63
H(2)	10232	5477	2279	77
H(3)	11064	4752	1036	70
H(4)	9770	-242	1875	69
H(5)	11896	-433	1490	86
H(6)	12050	1164	532	74
H(7)	5465	1960	-969	59
H(8)	6176	2619	-2284	70
H(9)	8546	3062	-1732	67
H(12A)	7811	2471	4292	115
H(12B)	8914	1556	4491	115
H(12C)	7400	1228	4252	115
H(13)	6239	4309	768	79
H(14)	4218	4876	1160	92
H(15)	3263	3185	1648	96
H(16)	4697	1650	1498	88
H(1A)	10500(50)	2970(40)	-90(30)	60