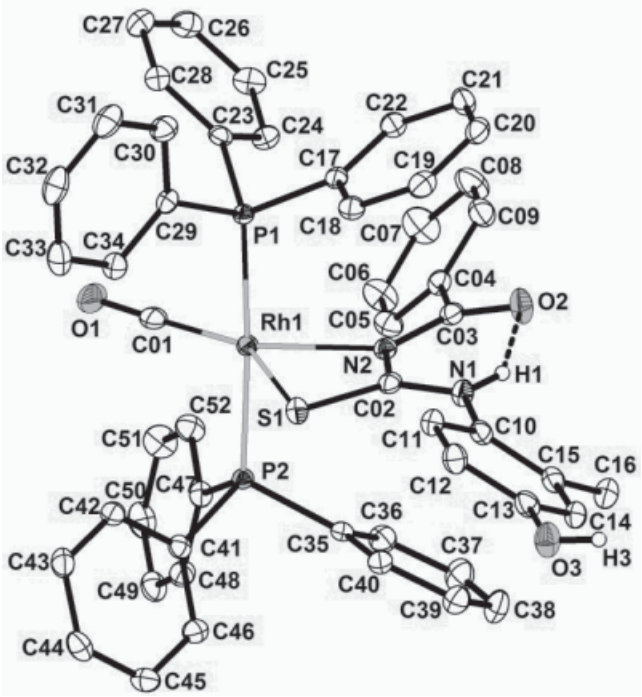
Crystal structure of bis(triphenylphosphine)(carbonyl)(*N*-benzoyl-*N*'-(2-methyl-4-hydroxyphenyl)thioureato-κ*S*,κ*N*)rhodium(I), $C_{52}H_{43}N_2O_3P_2RhS$

Stefan Warsink[*, I], Andreas Roodt[I], Johan A. Venter[I], P. D. Riekert Kotze[II] and Stefanus Otto[II]

[I] Department of Chemistry and the Materials and Nanosciences Research Cluster, University of the Free State, PO Box 339, Bloemfontein, South Africa
[II] Sasol Technology, R&D division, 1 Klasie Havenga Street, Sasolburg 1948, South Africa

Received January 23, 2013, accepted June 13, 2013, available online June 28, 2013, CCDC no. 1267/4002



Abstract

$C_{52}H_{43}N_2O_3P_2RhS$, triclinic, $P\bar{1}$ (no. 2), a = 10.6260(3) Å, b = 11.7305(3) Å, c = 19.6582(5) Å, α = 76.489(1)°, β = 82.027(1)°, γ = 64.848(1)°, V = 2154.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.028, $wR_{ref}(F^2)$ = 0.0722, T = 100 K.

Table 1. Data collection and handling.

Crystal:	orange platelets, size 0.05×0.16×0.28 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	5.67 cm^{-1}
Diffractometer, scan mode:	Bruker X8 ApexII κ CCD, φ and ω
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	46778, 10329
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 8979
$N(param)_{refined}$:	556
Programs:	SAINT-Plus [10], SIR-97 [11], SHELX [12] MERCURY [13], WinGX [14], SADABS [15]

Source of material

To a cold DMF solution (5 mL) of $[Rh(\mu\text{-}Cl)(CO)_2]_2$ (30 mg, 0.1028 mmol) 2 equivalents of *N*-benzoyl-*N*'-(4-hydroxy-2-methylphenyl)thiourea were added [9]. After 4 minutes of stirring, ice-cold water was added to precipitate a dark-red solid. After isolating the solid, it was taken up in diethyl ether and treated with 4 equivalents of triphenylphosphine. The solvent was allowed to evaporate slowly, yielding the title compound as bright orange crystals.

Discussion

In our ongoing research in bidentate ligand systems, we have investigated the use of thiourea (*tu*) ligands for the synthesis of rhodium complexes, amongst others [1-4]. These ligands show exceptional coordination behaviour, being able to coordinate through their sulfur atom alone as a neutral monodentate ligand [5,6], through their sulfur and oxygen atoms as a monoanionic bidentate ligand [7], and as a monoanionic bidentate ligand through its sulfur and one of its nitrogen atoms (this work). This four-membered chelate ring has a very small bite angle of 63.06 (4)°, whereas the bite angle of the *S,O*-coordination mode is much closer to the preferred 90° for square planar coordination to rhodium(I) [8]. The coordination in the title compound can be described as distorted trigonal bipyrimidal, with the two triphenylphosphine ligands in the apical positions. Alternatively, the *N,S*-thioureato ligand can be considered as one donating moiety, in which case the complex can be described as distorted square planar. The rhodium-ligand bond lengths are all within expected ranges; the Rh–S and Rh–N bond lengths are 2.623(1) and 2.278(2) Å, respectively. The C–O bond length within the carbonyl ligand is 1.158(2) Å, while it is coordinated in an almost linear fashion, with a Rh1–C01–O1 angle of 176.9(2)°. The solid state structure is stabilized by both intra- and intermolecular hydrogen bonds. The intramolecular bond is between the N1 hydrogen and O2 (1.88(2) Å), whereas the intermolecular ones link two molecules together in a dimeric fashion from the phenolic hydrogen to the benzoyl oxygen (O2–H2···O3, 1.99 Å).

* Correspondence author (e-mail: 2011009426@ufs4life.ac.za)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(05)	2*i*	0.3336	–0.0292	0.6929	0.024
H(06)	2*i*	0.1920	–0.1399	0.7037	0.032
H(07)	2*i*	–0.0341	–0.0326	–0.0326	0.038
H(08)	2*i*	–0.1183	0.1851	0.6133	0.035
H(09)	2*i*	0.0257	0.2948	0.5980	0.027
H(11)	2*i*	0.5728	0.4229	0.6953	0.022
H(12)	2*i*	0.7268	0.5225	0.6608	0.024
H(14)	2*i*	0.7751	0.4360	0.4687	0.022
H(16A)	2*i*	0.5236	0.3612	0.4647	0.031
H(16B)	2*i*	0.6178	0.2232	0.5079	0.031
H(16C)	2*i*	0.6867	0.2956	0.4453	0.031
H(18)	2*i*	0.3201	0.4443	0.7752	0.021
H(19)	2*i*	0.2672	0.6296	0.6883	0.024
H(20)	2*i*	0.0696	0.7056	0.6237	0.026
H(21)	2*i*	–0.0710	0.5926	0.6433	0.026
H(22)	2*i*	–0.0188	0.4058	0.7295	0.022
H(24)	2*i*	0.0529	0.1598	0.7727	0.022
H(25)	2*i*	–0.1472	0.1209	0.8051	0.027
H(26)	2*i*	–0.2676	0.1636	0.9113	0.027
H(27)	2*i*	–0.1910	0.2499	0.9839	0.027
H(28)	2*i*	0.0040	0.2972	0.9501	0.022
H(30)	2*i*	0.0692	0.4817	0.8957	0.024
H(31)	2*i*	0.1248	0.5544	0.9834	0.030
H(32)	2*i*	0.3350	0.4366	1.0384	0.032
H(33)	2*i*	0.4900	0.2434	1.0071	0.030
H(34)	2*i*	0.4345	0.1667	0.9208	0.022
H(36)	2*i*	0.5463	–0.2198	0.6657	0.024
H(37)	2*i*	0.6098	–0.2068	0.5466	0.032
H(38)	2*i*	0.7404	–0.0899	0.4932	0.034
H(39)	2*i*	0.8038	0.0176	0.5590	0.028
H(40)	2*i*	0.7332	0.0122	0.6770	0.021
H(42)	2*i*	0.6241	–0.0587	0.9036	0.020
H(43)	2*i*	0.8172	–0.0985	0.9640	0.024
H(44)	2*i*	1.0417	–0.1980	0.9155	0.027
H(45)	2*i*	1.0715	–0.2647	0.8093	0.027
H(46)	2*i*	0.8792	–0.2277	0.7495	0.022
H(48)	2*i*	0.7631	–0.3744	0.7895	0.022
H(49)	2*i*	0.7395	–0.5689	0.8166	0.026
H(50)	2*i*	0.5206	–0.5722	0.8484	0.029
H(51)	2*i*	0.3249	–0.3802	0.8487	0.032
H(52)	2*i*	0.3463	–0.1838	0.8191	0.025
H(3)	2*i*	0.8446	0.5866	0.5002	0.037
H(1)	2*i*	0.431(3)	0.324(2)	0.589(1)	0.028(6)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(01)	2*i*	0.3390(2)	–0.0080(2)	0.8790(1)	0.018(1)	0.0134(8)	0.0212(9)	–0.0001(7)	0.0019(7)	–0.0025(7)
C(02)	2*i*	0.4670(2)	0.2373(2)	0.68028(9)	0.0155(9)	0.0116(7)	0.0144(8)	–0.0035(7)	0.0016(7)	–0.0044(6)
C(03)	2*i*	0.2841(2)	0.2153(2)	0.63435(9)	0.0153(9)	0.0156(8)	0.0149(8)	–0.0051(7)	0.0016(7)	–0.0045(7)
C(04)	2*i*	0.1931(2)	0.1439(2)	0.64485(9)	0.0176(9)	0.0184(8)	0.0136(8)	–0.0078(7)	0.0002(7)	–0.0041(7)
C(05)	2*i*	0.2421(2)	0.0144(2)	0.6762(1)	0.018(1)	0.0174(9)	0.0237(9)	–0.0059(8)	–0.0036(8)	–0.0052(7)
C(06)	2*i*	0.1577(2)	–0.0511(2)	0.6832(1)	0.026(1)	0.0186(9)	0.036(1)	–0.0109(9)	–0.0073(9)	–0.0021(8)
C(07)	2*i*	0.0241(2)	0.0123(2)	0.6602(1)	0.029(1)	0.032(1)	0.042(1)	–0.019(1)	–0.008(1)	–0.002(1)
C(08)	2*i*	–0.0259(2)	0.1416(2)	0.6289(1)	0.020(1)	0.031(1)	0.036(1)	–0.0105(9)	–0.0099(9)	0.0012(9)
C(09)	2*i*	0.0589(2)	0.2070(2)	0.6205(1)	0.021(1)	0.0214(9)	0.0217(9)	–0.0074(8)	–0.0035(8)	0.0010(7)
C(10)	2*i*	0.5836(2)	0.3685(2)	0.60273(9)	0.0146(9)	0.0149(8)	0.0160(8)	–0.0060(7)	–0.0027(7)	0.0011(7)
C(11)	2*i*	0.6142(2)	0.4252(2)	0.64927(9)	0.020(1)	0.0190(8)	0.0144(8)	–0.0080(8)	0.0000(7)	–0.0009(7)
C(12)	2*i*	0.7048(2)	0.4851(2)	0.6287(1)	0.023(1)	0.0212(9)	0.0174(9)	–0.0114(8)	–0.0045(7)	–0.0025(7)
C(13)	2*i*	0.7635(2)	0.4903(2)	0.5610(1)	0.017(1)	0.0179(8)	0.0199(9)	–0.0082(8)	–0.0036(7)	0.0020(7)
C(14)	2*i*	0.7338(2)	0.4329(2)	0.51477(9)	0.020(1)	0.0195(9)	0.0139(8)	–0.0077(8)	–0.0001(7)	0.0015(7)
C(15)	2*i*	0.6443(2)	0.3706(2)	0.53472(9)	0.019(1)	0.0148(8)	0.0161(8)	–0.0053(7)	–0.0035(7)	0.0001(7)
C(16)	2*i*	0.6156(2)	0.3071(2)	0.48366(9)	0.027(1)	0.0211(9)	0.0153(8)	–0.0114(8)	0.0005(8)	–0.0030(7)
C(17)	2*i*	0.1550(2)	0.4068(2)	0.76161(9)	0.0168(9)	0.0103(7)	0.0132(8)	–0.0025(7)	0.0010(7)	–0.0030(6)
C(18)	2*i*	0.2402(2)	0.4742(2)	0.74859(9)	0.0171(9)	0.0148(8)	0.0186(9)	–0.0044(7)	0.0000(7)	–0.0046(7)
C(19)	2*i*	0.2085(2)	0.5846(2)	0.6970(1)	0.023(1)	0.0159(8)	0.0205(9)	–0.0082(8)	0.0042(8)	–0.0043(7)
C(20)	2*i*	0.0921(2)	0.6292(2)	0.65837(9)	0.027(1)	0.0146(8)	0.0153(9)	–0.0027(8)	0.0032(8)	–0.0015(7)
C(21)	2*i*	0.0084(2)	0.5624(2)	0.6704(1)	0.023(1)	0.0213(9)	0.0165(9)	–0.0025(8)	–0.0057(8)	–0.0031(7)
C(22)	2*i*	0.0392(2)	0.4512(2)	0.72174(9)	0.018(1)	0.0180(8)	0.0175(9)	–0.0058(8)	–0.0005(7)	–0.0048(7)
C(23)	2*i*	0.0476(2)	0.2351(2)	0.85764(9)	0.0117(9)	0.0108(7)	0.0171(8)	–0.0020(7)	–0.0012(7)	–0.0008(6)
C(24)	2*i*	0.0024(2)	0.1802(2)	0.8152(1)	0.018(1)	0.0181(8)	0.0188(9)	–0.0061(8)	0.0020(7)	–0.0071(7)
C(25)	2*i*	–0.1156(2)	0.1556(2)	0.8349(1)	0.019(1)	0.0200(9)	0.030(1)	–0.0086(8)	–0.0016(8)	–0.0077(8)
C(26)	2*i*	–0.1875(2)	0.1814(2)	0.8978(1)	0.017(1)	0.0205(9)	0.029(1)	–0.0099(8)	0.0021(8)	–0.0014(8)
C(27)	2*i*	–0.1423(2)	0.2331(2)	0.9406(1)	0.021(1)	0.027(1)	0.0194(9)	–0.0100(8)	0.0037(8)	–0.0044(8)
C(28)	2*i*	–0.0257(2)	0.2607(2)	0.92060(9)	0.0167(9)	0.0191(8)	0.0169(8)	–0.0062(7)	–0.0006(7)	–0.0032(7)
C(29)	2*i*	0.2457(2)	0.3156(2)	0.89977(9)	0.0168(9)	0.0154(8)	0.0125(8)	–0.0082(7)	0.0018(7)	–0.0026(6)
C(30)	2*i*	0.1544(2)	0.4322(2)	0.9185(1)	0.021(1)	0.0178(8)	0.0199(9)	–0.0070(8)	0.0020(8)	–0.0059(7)
C(31)	2*i*	0.1880(2)	0.4759(2)	0.9704(1)	0.035(1)	0.024(1)	0.0204(9)	–0.0149(9)	0.0056(9)	–0.0111(8)
C(32)	2*i*	0.3125(2)	0.4059(2)	1.0032(1)	0.041(1)	0.033(1)	0.0162(9)	–0.024(1)	0.0011(9)	–0.0076(8)
C(33)	2*i*	0.4041(2)	0.2913(2)	0.9847(1)	0.029(1)	0.032(1)	0.0174(9)	–0.0177(9)	–0.0061(8)	0.0006(8)
C(34)	2*i*	0.3711(2)	0.2458(2)	0.93319(9)	0.019(1)	0.0190(8)	0.0165(8)	–0.0083(8)	–0.0006(7)	–0.0026(7)
C(35)	2*i*	0.6333(2)	–0.1051(2)	0.68367(9)	0.0119(9)	0.0138(8)	0.0147(8)	–0.0004(7)	–0.0007(7)	–0.0029(6)
C(36)	2*i*	0.5975(2)	–0.1703(2)	0.6441(1)	0.021(1)	0.0196(9)	0.0206(9)	–0.0076(8)	–0.0013(8)	–0.0049(7)
C(37)	2*i*	0.6363(2)	–0.1634(2)	0.5734(1)	0.033(1)	0.030(1)	0.021(1)	–0.012(1)	–0.0031(9)	–0.0103(8)
C(38)	2*i*	0.7132(2)	–0.0937(2)	0.5415(1)	0.034(1)	0.033(1)	0.0144(9)	–0.010(1)	0.0014(8)	–0.0056(8)
C(39)	2*i*	0.7501(2)	–0.0296(2)	0.5805(1)	0.023(1)	0.0239(9)	0.0196(9)	–0.0088(8)	0.0022(8)	–0.0026(7)
C(40)	2*i*	0.7092(2)	–0.0339(2)	0.65095(9)	0.018(1)	0.0164(8)	0.0164(8)	–0.0045(7)	–0.0006(7)	–0.0039(7)
C(41)	2*i*	0.7314(2)	–0.1379(2)	0.82017(9)	0.0154(9)	0.0119(7)	0.0153(8)	–0.0057(7)	–0.0012(7)	–0.0006(6)
C(42)	2*i*	0.7150(2)	–0.1006(2)	0.88420(9)	0.0170(9)	0.0146(8)	0.0166(8)	–0.0045(7)	–0.0001(7)	–0.0026(7)
C(43)	2*i*	0.8297(2)	–0.1237(2)	0.9201(1)	0.025(1)	0.0198(9)	0.0148(8)	–0.0081(8)	–0.0034(7)	–0.0022(7)

Table 3. continued.

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(44)	2*i*	0.9628(2)	–0.1837(2)	0.8916(1)	0.020(1)	0.0236(9)	0.0223(9)	–0.0082(8)	–0.0084(8)	0.0004(8)
C(45)	2*i*	0.9803(2)	–0.2225(2)	0.8284(1)	0.015(1)	0.0230(9)	0.025(1)	–0.0043(8)	–0.0001(8)	–0.0036(8)
C(46)	2*i*	0.8661(2)	–0.2003(2)	0.7928(1)	0.017(1)	0.0187(8)	0.0181(9)	–0.0055(7)	0.0001(7)	–0.0053(7)
C(47)	2*i*	0.5571(2)	–0.2591(2)	0.80174(9)	0.020(1)	0.0122(8)	0.0145(8)	–0.0067(7)	–0.0015(7)	–0.0028(6)
C(48)	2*i*	0.6736(2)	–0.3750(2)	0.80129(9)	0.020(1)	0.0167(8)	0.0177(9)	–0.0070(8)	0.0008(7)	–0.0034(7)
C(49)	2*i*	0.6598(2)	–0.4908(2)	0.8178(1)	0.028(1)	0.0144(8)	0.0191(9)	–0.0055(8)	–0.0042(8)	–0.0021(7)
C(50)	2*i*	0.5298(2)	–0.4928(2)	0.8362(1)	0.035(1)	0.0176(9)	0.024(1)	–0.0151(9)	–0.0069(9)	0.0016(7)
C(51)	2*i*	0.4140(2)	–0.3789(2)	0.8365(1)	0.026(1)	0.025(1)	0.033(1)	–0.0162(9)	–0.0020(9)	–0.0026(8)
C(52)	2*i*	0.4268(2)	–0.2618(2)	0.8191(1)	0.020(1)	0.0170(9)	0.025(1)	–0.0076(8)	–0.0022(8)	–0.0020(7)
N(1)	2*i*	0.4857(2)	0.3119(1)	0.62047(8)	0.0188(8)	0.0190(7)	0.0129(7)	–0.0102(7)	–0.0008(6)	–0.0011(6)
N(2)	2*i*	0.3734(2)	0.1833(1)	0.68550(7)	0.0141(8)	0.0129(7)	0.0140(7)	–0.0046(6)	0.0008(6)	–0.0032(5)
O(1)	2*i*	0.3055(2)	–0.0589(1)	0.93161(7)	0.0325(9)	0.0236(7)	0.0249(7)	–0.0038(7)	0.0088(6)	0.0044(6)
O(2)	2*i*	0.2719(2)	0.2989(1)	0.57986(7)	0.0293(8)	0.0290(7)	0.0177(6)	–0.0181(6)	–0.0069(6)	0.0051(5)
O(3)	2*i*	0.8535(2)	0.5497(1)	0.54249(7)	0.0275(8)	0.0334(8)	0.0195(7)	–0.0212(7)	–0.0035(6)	0.0026(6)
P(1)	2*i*	0.20718(5)	0.25966(4)	0.82935(2)	0.0117(2)	0.0106(2)	0.0118(2)	–0.0035(2)	0.0003(2)	–0.0024(2)
P(2)	2*i*	0.57573(5)	–0.10611(4)	0.77608(2)	0.0123(2)	0.0109(2)	0.0124(2)	–0.0040(2)	0.0005(2)	–0.0026(2)
S(1)	2*i*	0.55264(5)	0.19844(4)	0.75508(2)	0.0193(2)	0.0165(2)	0.0138(2)	–0.0075(2)	–0.0022(2)	–0.0010(2)
Rh(1)	2*i*	0.38792(1)	0.07898(1)	0.799384(7)	0.01243(8)	0.01041(7)	0.01185(7)	–0.00386(5)	0.00071(5)	–0.00164(5)

Acknowledgments. The authors thank SASOL, the South African NRF and THRIP, the University of the Free State Research Fund and the UFS Materials and Nanosciences Strategic Research Cluster initiative for financial support. The views expressed do not necessarily represent those of the NRF.

References

1. Roodt, A.; Steyl, G.: Structure and solution behaviour of rhodium(I) Vaska-type complexes for correlation of steric and electronic properties of tertiary phosphine ligands. Coord. Chem. Rev. **245** (2003) 121-137.
2. Roodt, A.; Visser, H. G.; Brink, A.: Structure/reactivity relationships and mechanism from X-ray data and spectroscopic kinetic analysis. Crystallogr. Rev. **17** (2011) 241-280.
3. Brink, A.; Roodt, A.; Steyl, G.; Visser, H. G.: Steric vs. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [$PR_3 = PPh_3$, PPh_2Cy, $PPhCy_2$ and PCy_3]. Dalton Trans. (2010) 5572-5578.
4. Schutte, M.; Roodt, A.; Visser, H. G.: Coordinated Aqua vs Methanol Substitution Kinetics in *fac*-Re(I) Tricarbonyl Tropolonato Complexes. Inorg. Chem. **51** (2012) 11996-12006.
5. Kotze, P. D. R.; Roodt, A.; Venter, J. A.; Otto, S.: (*N*-Benzoyl-*N*'-phenylthiourea-κ*S*)chlorido(η^4-1,5-cyclooctadiene)rhodium(I). Acta Crystallogr. **E66** (2010) m1028-m1029.
6. unpublished results.
7. Warsink, S.; Roodt, A.: (*N*-Benzoyl-*N*',*N*'-diphenylthioureato-$\kappa^2 S,O$)(η^4-cycloocta-1,5-diene)rhodium(I). Acta Crystallogr. **E68** (2012) m1053-m1054.
8. unpublished results.
9. Douglass, I. B.; Dains, F. B.: Some Derivatives of Benzoyl and Furoyl Isothiocyanates and their Use in Synthesizing Heterocyclic Compounds. J. Am. Chem. Soc. **56** (1934) 719-721.
10. Bruker (2007). APEX2, SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
11. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. J. Appl. Crystallogr. **32** (1999) 115-119.
12. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.
13. Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P.A.: Mercury CSD 2.0 – new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. **41** (2008) 466-470.
14. Farrugia, L. J.: WinGX and ORTEP for Windows: an update. J. Appl. Crystallogr. **45** (2012) 849-854.
15. Bruker (2001). SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.