Wisdom Ebong, Alexandra E. Muniz, David R. Khan, Daniel K. Unruh and Jason C. Yarbrough*

Synthesis and crystal structure of nonacarbonyltris[(2-thia-1,3,5-triaza-7-phosphatricylco[3.3.1.1]decane- κ^1P)-2,2-dioxide]triruthenium(0) – acetonitrile (7/6), $C_{25.71}H_{32.57}N_{9.86}O_{15}P_3S_3Ru_3$

*Corresponding author: Jason C. Yarbrough, Department of Chemistry & Physics, West Texas A&M University, WTAMU Box 60732, Canyon, TX 79016-0001, USA, E-mail: jyarbrough@wtamu.edu. <https://orcid.org/0000-0002-1893-2856>

Wisdom Ebong, Alexandra E. Muniz and David R. Khan, Department of Chemistry & Physics, West Texas A&M University, WTAMU Box 60732, Canyon, TX 79016-0001, USA, E-mail: wisdomebong@mail.rossmed.edu (W. Ebong), amuniz@wtamu.edu (A.E. Muniz), dkhan@wtamu.edu (D.R. Khan)

Daniel K. Unruh, Department of Chemistry & Biochemistry, Texas Tech University, 1204 Boston Ave., Lubock, TX 79409-1061, USA, E-mail: daniel.unruh@ttu.edu

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Abstract

$C_{25.71}H_{32.57}N_{9.86}O_{15}P_3S_3Ru_3$, hexagonal, $P6_3$ (no. 173), $a = 37.24213(9)$ Å, $b = 37.24213(9)$ Å, $c = 11.64828(3)$ Å, $\beta = 90^\circ$, $V = 13,991.40(8)$ Å³, $Z = 14$, $R_{\text{gt}}(F) = 0.0406$, $wR_{\text{ref}}(F^2) = 0.1009$, $T = 100(2)$ K.

CCDC no.: 2117216

Table 1: Data collection and handling.

Crystal:	Orange column
Size:	$0.18 \times 0.06 \times 0.05$ mm
Wavelength:	Cu $K\alpha$ radiation (1.54178 Å)
μ :	12.4 mm^{-1}
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	77.4° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	180,987, 19,572, 0.049
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 19,241
$N(\text{param})_{\text{refined}}$:	1254
Programs:	CrysAlis ^{PRO} [1], SCALE3 ABSPACK [2], SHELX [3, 4], OLEX2 [5]

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The phosphine ligand, 2-thia-1,3,5-triaza-7-phosphadamantane-2,2-dioxide (PASO₂), was prepared according to previously published procedures [6, 7]. The title compound was obtained by combining 0.360 g (0.56 mmol) triruthenium dodecacarbonyl with 0.154 g (0.743 mmol) PASO₂ in 130 ml of xylene. The resulting red solution was refluxed with stirring for 16 h under argon. The solution was then passed through alumina and the solvent removed in vacuo to yield an orange crystalline powder. Clear orange crystals suitable for X-ray diffraction were obtained *via* solvent diffusion, where a solution of the title compound in acetonitrile was layered with a two-fold excess of dichloromethane and allowed to sit for four weeks at reduced temperature (approximately 263 K).

Experimental details

Data were collected on a Rigaku XtaLAB Synergy-*i* Kappa diffractometer equipped with a PhotonJet-*i* X-ray source operated at 50 W (50 kV, 1 mA) to generate Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) and a HyPix-6000HE HPC detector. The SHELX-2014 series of programs was used for the solution and refinement of the crystal structure [3, 4]. Hydrogen atoms bound to carbon atoms were geometrically constrained and refined by the riding model. For all H atoms, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$ of the carrier atom was assumed (1.5 in the case of methyl groups). The absolute structure was determined by anomalous scattering.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ru1	0.27257 (2)	0.19371 (2)	0.70735 (4)	0.03148 (10)
Ru2	0.18429 (2)	0.15030 (2)	0.70543 (4)	0.03215 (10)
Ru3	0.22916 (2)	0.23868 (2)	0.68830 (4)	0.03202 (10)
Ru4	0.47266 (2)	0.57221 (2)	0.50526 (4)	0.03336 (10)
Ru5	0.51829 (2)	0.65985 (2)	0.53670 (4)	0.03386 (10)
Ru6	0.56126 (2)	0.61429 (2)	0.51118 (4)	0.03300 (10)
Ru7	0.62640 (2)	0.34074 (2)	0.51535 (5)	0.04027 (11)
N7	0.36082 (15)	0.36315 (15)	0.5815 (5)	0.0366 (10)
S1	0.33708 (5)	0.10820 (5)	0.49979 (14)	0.0387 (3)
S2	0.02883 (4)	0.09322 (4)	0.52727 (13)	0.0368 (3)
S3	0.35897 (4)	0.39835 (4)	0.66440 (13)	0.0353 (3)
S4	0.31704 (4)	0.52069 (4)	0.67086 (14)	0.0382 (3)
S5	0.64719 (4)	0.82043 (4)	0.54765 (13)	0.0358 (3)
S6	0.61842 (5)	0.51739 (5)	0.68897 (15)	0.0423 (3)
S7	0.47674 (5)	0.25030 (5)	0.71995 (15)	0.0434 (3)
P1	0.29004 (4)	0.14413 (4)	0.66921 (13)	0.0330 (3)
P2	0.11724 (4)	0.13591 (4)	0.67513 (13)	0.0330 (3)
P3	0.27873 (4)	0.30363 (4)	0.62768 (13)	0.0326 (3)
P4	0.40686 (4)	0.56150 (4)	0.53102 (13)	0.0348 (3)
P5	0.56906 (4)	0.72507 (4)	0.58947 (14)	0.0347 (3)
P6	0.57609 (4)	0.56198 (4)	0.53439 (13)	0.0340 (3)
P7	0.55874 (5)	0.29156 (5)	0.54823 (15)	0.0412 (3)
O1	0.25253 (15)	0.16052 (15)	0.9546 (4)	0.0435 (10)
O2	0.28614 (15)	0.21715 (16)	0.4524 (4)	0.0458 (10)
O3	0.35954 (14)	0.25987 (13)	0.7772 (4)	0.0428 (9)
O4	0.17622 (14)	0.17737 (14)	0.9491 (4)	0.0407 (9)
O5	0.19897 (15)	0.13569 (15)	0.4542 (4)	0.0432 (10)
O6	0.16952 (15)	0.06485 (13)	0.7674 (4)	0.0428 (10)
O7	0.26443 (14)	0.25530 (14)	0.9334 (4)	0.0397 (9)
O8	0.19951 (14)	0.21894 (14)	0.4375 (4)	0.0420 (9)
N8	0.31079 (15)	0.38925 (15)	0.6464 (5)	0.0361 (10)
O9	0.16083 (14)	0.25636 (15)	0.7586 (5)	0.0436 (10)
N9	0.30734 (17)	0.36055 (16)	0.4510 (5)	0.0397 (11)
O10	0.35054 (16)	0.07864 (15)	0.4849 (4)	0.0452 (10)
N10	0.32248 (16)	0.50218 (16)	0.5471 (5)	0.0387 (10)
O11	0.34402 (16)	0.13743 (15)	0.4124 (4)	0.0453 (10)
N11	0.34888 (15)	0.57146 (16)	0.6593 (5)	0.0380 (10)
O12	−0.01285 (13)	0.08509 (14)	0.5215 (4)	0.0418 (9)
N12	0.34095 (15)	0.56794 (17)	0.4469 (5)	0.0388 (11)
O13	0.04548 (15)	0.08046 (16)	0.4358 (5)	0.0469 (10)
N13	0.60053 (15)	0.78165 (15)	0.7667 (5)	0.0361 (10)
O14	0.36307 (14)	0.38950 (13)	0.7812 (4)	0.0412 (9)
N14	0.65164 (15)	0.78524 (15)	0.6247 (5)	0.0360 (10)
O15	0.38654 (14)	0.43817 (13)	0.6172 (5)	0.0427 (10)
C15	0.46071 (18)	0.51778 (19)	0.4629 (6)	0.0383 (12)
N15	0.59927 (15)	0.81047 (15)	0.5761 (5)	0.0356 (10)
N1	0.35826 (17)	0.13400 (17)	0.6207 (5)	0.0394 (10)
N2	0.30019 (18)	0.07891 (17)	0.7355 (5)	0.0414 (11)
N3	0.28686 (16)	0.08215 (15)	0.5288 (5)	0.0391 (10)
N4	0.04855 (16)	0.13782 (16)	0.7538 (5)	0.0378 (10)
N5	0.03428 (15)	0.07410 (16)	0.6489 (5)	0.0366 (10)
N6	0.05885 (16)	0.14406 (16)	0.5431 (5)	0.0379 (10)
C1	0.25802 (18)	0.17329 (19)	0.8636 (6)	0.0377 (12)
C2	0.27899 (18)	0.20916 (18)	0.5467 (6)	0.0367 (12)
C3	0.32728 (18)	0.23556 (17)	0.7478 (5)	0.0346 (11)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C4	0.18108 (17)	0.16907 (17)	0.8591 (6)	0.0360 (12)
C5	0.19451 (18)	0.14229 (18)	0.5465 (6)	0.0378 (12)
C6	0.17424 (18)	0.09692 (19)	0.7458 (6)	0.0379 (12)
C7	0.25228 (17)	0.24765 (17)	0.8422 (6)	0.0349 (11)
C8	0.21010 (17)	0.22416 (17)	0.5311 (6)	0.0357 (11)
C9	0.18674 (18)	0.25058 (18)	0.7296 (6)	0.0363 (12)
C10	0.34634 (18)	0.16589 (18)	0.6429 (6)	0.0363 (11)
H10A	0.354615	0.184822	0.576081	0.044*
H10B	0.361912	0.182489	0.710462	0.044*
C11	0.2823 (2)	0.10433 (19)	0.7754 (6)	0.0382 (12)
H11A	0.295556	0.117927	0.848744	0.046*
H11B	0.252295	0.086147	0.789555	0.046*
C12	0.26837 (18)	0.10940 (18)	0.5430 (6)	0.0365 (11)
H12A	0.237971	0.091907	0.552189	0.044*
H12B	0.273713	0.12639	0.472978	0.044*
C13	0.3450 (2)	0.1033 (2)	0.7185 (6)	0.0438 (13)
H13A	0.355636	0.084105	0.704025	0.053*
H13B	0.357939	0.118572	0.790216	0.053*
C14	0.2801 (2)	0.05580 (19)	0.6326 (6)	0.0428 (13)
H14A	0.249887	0.038977	0.647192	0.051*
H14B	0.290339	0.036429	0.616038	0.051*
C16	0.07695 (17)	0.08037 (18)	0.6626 (6)	0.0363 (11)
H16A	0.083383	0.068196	0.595636	0.044*
H16B	0.077722	0.065471	0.732092	0.044*
N16	0.56799 (17)	0.49485 (16)	0.6628 (5)	0.0406 (11)
O16	0.48419 (16)	0.55426 (16)	0.7565 (5)	0.0473 (10)
C17	0.10391 (18)	0.15685 (19)	0.5479 (6)	0.0389 (12)
H17A	0.120629	0.187498	0.549311	0.047*
H17B	0.111331	0.147125	0.477531	0.047*
N17	0.57932 (17)	0.49425 (16)	0.4535 (5)	0.0400 (11)
O17	0.46609 (14)	0.59873 (14)	0.2596 (4)	0.0425 (10)
C18	0.09169 (18)	0.15113 (19)	0.7848 (6)	0.0378 (12)
H18A	0.092137	0.138588	0.859339	0.045*
H18B	0.107325	0.181639	0.793953	0.045*
N18	0.63968 (16)	0.54398 (17)	0.5705 (5)	0.0397 (11)
O18	0.45614 (15)	0.48648 (14)	0.4373 (5)	0.0439 (10)
C19	0.02301 (18)	0.09283 (19)	0.7474 (6)	0.0390 (12)
H19A	−0.0064	0.085324	0.73951	0.047*
H19B	0.025808	0.08071	0.820149	0.047*
N19	0.49880 (18)	0.22396 (18)	0.6723 (6)	0.0470 (12)
O19	0.49182 (16)	0.64037 (15)	0.7889 (5)	0.0477 (10)
C20	0.04550 (19)	0.15728 (19)	0.6506 (6)	0.0398 (12)
H20A	0.06288	0.187713	0.659123	0.048*
H20B	0.016414	0.150677	0.640978	0.048*
N20	0.48096 (19)	0.28078 (19)	0.6111 (5)	0.0451 (12)
O20	0.44937 (14)	0.68014 (14)	0.5063 (5)	0.0476 (11)
C21	0.33455 (18)	0.32017 (18)	0.6278 (6)	0.0366 (11)
H21A	0.343365	0.319103	0.707353	0.044*
H21B	0.338978	0.30057	0.580859	0.044*
N21	0.4819 (2)	0.2307 (2)	0.4711 (6)	0.0524 (14)
O21	0.57471 (16)	0.63320 (18)	0.7701 (5)	0.0490 (11)
C22	0.2752 (2)	0.31776 (19)	0.4777 (5)	0.0399 (12)
H22A	0.278187	0.298518	0.425088	0.048*
H22B	0.247543	0.31467	0.464661	0.048*
N22	0.3148 (2)	0.2842 (2)	0.2374 (6)	0.0513 (14)
O22	0.54347 (16)	0.58749 (16)	0.2585 (4)	0.0467 (10)

Table 2: (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
C23	0.28010 (17)	0.34877 (17)	0.6982 (6)	0.0361 (11)
H23A	0.252182	0.345766	0.693561	0.043*
H23B	0.286866	0.348841	0.780387	0.043*
N23	0.6067 (2)	0.7132 (3)	0.9833 (7)	0.0642 (18)
O23	0.64966 (14)	0.67933 (14)	0.4492 (5)	0.0468 (11)
C24	0.30272 (19)	0.39094 (18)	0.5204 (6)	0.0404 (12)
H24A	0.274217	0.386058	0.510551	0.049*
H24B	0.32216	0.419109	0.491245	0.049*
O24	0.33143 (14)	0.50539 (14)	0.7607 (5)	0.0447 (10)
C25	0.3488 (2)	0.36703 (19)	0.4603 (6)	0.0404 (13)
H25A	0.368705	0.395015	0.430817	0.049*
H25B	0.35109	0.346545	0.411148	0.049*
O25	0.27592 (14)	0.51410 (14)	0.6731 (5)	0.0444 (10)
C26	0.36450 (17)	0.50675 (17)	0.5360 (6)	0.0371 (12)
H26A	0.365388	0.492552	0.46516	0.044*
H26B	0.369237	0.492837	0.601934	0.044*
O26	0.67483 (14)	0.86039 (14)	0.5943 (4)	0.0423 (10)
C27	0.38406 (18)	0.57976 (19)	0.4195 (6)	0.0371 (12)
H27A	0.400928	0.610313	0.413054	0.045*
H27B	0.384824	0.56772	0.344382	0.045*
O27	0.64927 (14)	0.81242 (14)	0.4294 (4)	0.0412 (9)
C28	0.39348 (18)	0.58203 (19)	0.6590 (6)	0.0377 (12)
H28A	0.399018	0.57053	0.729041	0.045*
H28B	0.411509	0.612549	0.661263	0.045*
O28	0.62811 (16)	0.54566 (17)	0.7812 (5)	0.0509 (11)
C29	0.33803 (18)	0.58714 (19)	0.5535 (6)	0.0398 (12)
H29A	0.309386	0.582032	0.561447	0.048*
H29B	0.356808	0.617488	0.54812	0.048*
O29	0.62862 (15)	0.48528 (16)	0.6959 (5)	0.0497 (11)
C30	0.31369 (19)	0.52328 (19)	0.4503 (6)	0.0414 (13)
H30A	0.316224	0.511381	0.376773	0.05*
H30B	0.284688	0.517229	0.456907	0.05*
O30	0.61432 (18)	0.32376 (19)	0.2565 (5)	0.0546 (12)
C31	0.56841 (19)	0.73870 (18)	0.7406 (6)	0.0377 (12)
H31A	0.540842	0.735077	0.759073	0.045*
H31B	0.572716	0.719524	0.789863	0.045*
O31	0.43394 (16)	0.22140 (17)	0.7355 (5)	0.0514 (11)
C32	0.56791 (17)	0.76985 (17)	0.5255 (6)	0.0358 (11)
H32A	0.572933	0.77034	0.441937	0.043*
H32B	0.539925	0.766235	0.536395	0.043*
O32	0.50132 (15)	0.27560 (16)	0.8122 (5)	0.0491 (11)
C33	0.62504 (18)	0.74269 (17)	0.5787 (6)	0.0361 (11)
H33A	0.630856	0.723195	0.621538	0.043*
H33B	0.632231	0.742082	0.497172	0.043*
O33	0.55090 (14)	0.67887 (14)	0.2879 (4)	0.0434 (10)
C34	0.47037 (17)	0.59034 (18)	0.3503 (6)	0.0363 (12)
O34	0.63399 (17)	0.35524 (18)	0.7762 (5)	0.0534 (12)
C35	0.48153 (19)	0.56259 (19)	0.6637 (6)	0.0388 (12)
O35	0.6139 (2)	0.41419 (19)	0.4726 (6)	0.0611 (14)
C36	0.50170 (18)	0.64539 (18)	0.6950 (6)	0.0403 (13)
C37	0.53883 (18)	0.66992 (17)	0.3796 (6)	0.0357 (11)
C38	0.47575 (18)	0.67301 (17)	0.5146 (6)	0.0380 (12)
C39	0.56763 (19)	0.6267 (2)	0.6738 (6)	0.0405 (13)
C40	0.61645 (18)	0.65579 (18)	0.4754 (6)	0.0380 (12)
C41	0.54788 (19)	0.59789 (19)	0.3517 (6)	0.0381 (12)
C42	0.59366 (18)	0.81126 (18)	0.7045 (6)	0.0373 (11)

Table 2: (continued)

Atom	x	y	z	U_{iso}^*/U_{eq}
H42A	0.613128	0.839441	0.73347	0.045*
H42B	0.565141	0.805524	0.720238	0.045*
C43	0.64185 (19)	0.7885 (2)	0.7492 (6)	0.0389 (12)
H43A	0.645177	0.76788	0.794712	0.047*
H43B	0.662131	0.81637	0.778234	0.047*
C44	0.55298 (19)	0.5254 (2)	0.6563 (6)	0.0396 (12)
H44A	0.559936	0.541379	0.728809	0.048*
H44B	0.522422	0.510181	0.648191	0.048*
C45	0.5648 (2)	0.52326 (19)	0.4207 (6)	0.0388 (12)
H45A	0.534604	0.50747	0.406348	0.047*
H45B	0.578716	0.537646	0.348742	0.047*
C46	0.63153 (19)	0.57915 (19)	0.5563 (6)	0.0385 (12)
H46A	0.64754	0.59611	0.489671	0.046*
H46B	0.64153	0.596975	0.6254	0.046*
C47	0.5583 (2)	0.4702 (2)	0.5539 (7)	0.0436 (13)
H47A	0.565905	0.448407	0.56416	0.052*
H47B	0.528049	0.456121	0.540311	0.052*
C48	0.6241 (2)	0.5156 (2)	0.4680 (6)	0.0423 (13)
H48A	0.637293	0.531996	0.397995	0.051*
H48B	0.632884	0.494598	0.475527	0.051*
C49	0.6333 (2)	0.3499 (2)	0.6797 (6)	0.0433 (13)
C50	0.6207 (2)	0.3293 (2)	0.3515 (6)	0.0459 (15)
C51	0.6194 (2)	0.3872 (2)	0.4911 (7)	0.0445 (14)
C52	0.5255 (2)	0.3132 (2)	0.5918 (7)	0.0445 (14)
H52A	0.536666	0.329266	0.663462	0.053*
H52B	0.526729	0.332516	0.531593	0.053*
C53	0.5444 (2)	0.2509 (2)	0.6595 (6)	0.0440 (13)
H53A	0.556654	0.233522	0.638964	0.053*
H53B	0.556368	0.264384	0.734037	0.053*
C54	0.5253 (2)	0.2574 (2)	0.4332 (6)	0.0477 (15)
H54A	0.525795	0.274568	0.367646	0.057*
H54B	0.536389	0.239662	0.406266	0.057*
C55	0.4630 (2)	0.2551 (3)	0.5049 (7)	0.0513 (15)
H55A	0.433048	0.236034	0.517422	0.062*
H55B	0.46592	0.273716	0.440629	0.062*
C56	0.4789 (2)	0.2027 (2)	0.5600 (8)	0.0522 (16)
H56A	0.492303	0.187044	0.533043	0.063*
H56B	0.449281	0.182569	0.573955	0.063*
C57	0.2895 (2)	0.2510 (2)	0.2216 (6)	0.0430 (13)
C58	0.2568 (2)	0.2081 (2)	0.2022 (7)	0.0474 (14)
H58A	0.244078	0.205923	0.126897	0.071*
H58B	0.235646	0.199805	0.262149	0.071*
H58C	0.268747	0.189928	0.204394	0.071*
C59	0.5798 (3)	0.6804 (3)	1.0045 (7)	0.0578 (19)
C60	0.5465 (3)	0.6399 (3)	1.0295 (7)	0.0602 (19)
H60A	0.528563	0.628758	0.96206	0.09*
H60B	0.530438	0.641339	1.094207	0.09*
H60C	0.557672	0.621851	1.049642	0.09*

Comment

The structural chemistry of metal-carbonyl cluster compounds and their derivatives has been an area of significant interest for many decades. This stems from their

application in a variety of endeavors, including heterogeneous catalyst design as well as materials chemistry and engineering research [8]. Indeed, many structural studies are reported in the literature and not surprisingly therefore, standard empirical rules have been established which make the geometry and stoichiometry of ligand binding reasonably predictable in such compounds [9–12]. Herein we report the synthesis and crystal structure of a solvated, triangulo-triruthenium compound, tri-substituted with the small, cage-like phosphine ligand, 2-thia-1,3,5-triaza-7-phosphaadamantane 2,2-dioxide ($PASO_2$), $Ru_3(CO)_9(PASO_2)_3 \cdot 6/7 C_2H_5N$. The synthesis of the title compound, $Ru_3(CO)_9(PASO_2)_3$, was accomplished by the thermal reaction of $Ru_3(CO)_{12}$ and the $PASO_2$ phosphine. Employing the crystallization method of solvent diffusion, the compound was found to crystallize into the non-centrosymmetric, hexagonal space group, $P6_3$. The asymmetric unit consists of 2 and 1/3 triruthenium clusters and two molecules of acetonitrile solvent. Further, each complex was determined to consist of a triangular Ru_3 core with interior bond angles of approximately 60° , ranging from $59.664(13)$ to $60.367(13)^\circ$ for the two crystallographically distinct Ru_3 cores in the asymmetric unit. Additionally, the corresponding Ru–Ru bond distances were all of similar length, ranging from $2.8473(5)$ to $2.8710(6)$ Å, consistent with the observed Ru–Ru bond lengths in the parent compound, $Ru_3(CO)_{12}$ which was previously reported in reference [13]. Furthermore, the crystallographically imposed bond angles and lengths corresponding to Ru7 are 60.0° and $2.8661(8)$ Å respectively. Analogous $Ru_3(CO)_9(PR_3)_3$ compounds reported previously [14–16] show similar bond lengths and angles with respect to the Ru_3 core. A thermal ellipsoid depiction of the title compound is shown in the figure. Each ruthenium bears three terminal carbonyl ligands and an equatorially positioned $PASO_2$ ligand, providing a somewhat distorted octahedral environment about each Ru center. The ruthenium–phosphorus bond lengths Ru1–P1, Ru2–P2, Ru3–P3, Ru4–P4, Ru5–P5, Ru6–P6 and Ru7–P7 are all fairly consistent and range from $2.2874(14)$ to $2.3042(14)$ Å. In all instances, the equatorial Ru–CO bond distances are shorter than those in the axial positions. These observations are consistent with the most analogous compound found in the chemical literature, $Ru_3(CO)_9(PTA)_3$ [15]. Additionally, and as expected with binding of the $PASO_2$ phosphine, the equatorial Ru–CO bond lengths are shorter than those in the structure of the unsubstituted parent compound, $Ru_3(CO)_{12}$ [13]. On this point, we can further note that binding of the phosphine ligands brings with it steric interactions which introduce significant distortion of the molecular symmetry from the D_{3h} molecular symmetry of $Ru_3(CO)_{12}$ to D_3 symmetry for the title

compound. This is readily observed in the Ru–Ru–CO_{ax} bond angles of the axial ligands, the average value of which is 78.6(9)° in contrast to that of roughly 90° for the parent compound, Ru₃(CO)₁₂ [13].

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