contacts must exist. There is a sudden change in solvate molecules from static to dynamic that occurs at the phase transition. Molecular mechanics calculations should be performed to evaluate with known crystallographic coordinates what potential fields the solvate molecules experiences in these M_3O complexes. There is a possibility that small van der Waals interactions (~50-100 cm^{-1}) between the M_3O and S molecules valence-trap the M_3O complexes.[6k]

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Synthesis and Structure of Dirhodium Compounds Featuring an End-On-Bridging Ditellurium

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The reaction of a polytellurides solution with $(np_3)Rh$ and $(pp_3)Rh$ cationic species [np_3 = tris(2-(diphenylphosphino)ethyl)amine, $N(CH_2CH_2PPh_2)_3$; pp_3 = tris(2-(diphenylphosphino)ethyl)phosphine, $P(CH_2CH_2PPh_2)_3$] yields the compounds $[LRh]_2Te_2{\cdot}THF$ [L = np_3 (**1**), pp_3 (**2**); THF = tetrahydrofuran]; the pp_3 derivative crystallizes also without solvent: $[(pp_3)Rh]_2Te_2$ (**3**). The polytellurides solution is easily prepared by reducing tellurium in aprotic solvents. The crystal structures of **1**-**3** were elucidated through complete X-ray analyses. The isomorphous compounds **1** and **2** crystallize in the monoclinic space group $P2_1/n$ with $Z = 2$ and the following lattice constants: (**1**) $a = 13.532$ (4) Å, $b = 19.669$ (6) Å, $c = 14.492$ (9) Å, $\beta = 91.89$ (7)°; (**2**) $a = 13.598$ (9) Å, $b = 20.243$ (6) Å, $c = 14.492$ (5) Å, $\beta = 92.55$ (4)°. Compound **3** is triclinic $P\bar{1}$, with $a = 13.543$ (2) Å, $b = 13.716$ (3) Å, $c = 13.370$ (4) Å, $\alpha = 111.65$ (2)°, $\beta = 95.62$ (2)°, $\gamma = 119.05$ (2)°, and $Z = 1$. All complexes contain a Te_2 unit end-on bound to two rhodium-ligand fragments forming a zigzag Rh-Te-Te-Rh chain. The isomorphous compounds **1** and **2** exhibit essentially identical [2.691 (2) Å] Te-Te distances. Changes in packing between the former compounds and **3** result in an appreciable change in that distance, which lengthens to 2.760 (1) Å.

Introduction

The chemistry of transition-metal compounds containing unsubstituted chalcogen atoms is currently opening new prospects in various fields. A rapidly growing class of chalcogen-rich metal compounds that exhibit unusual structural and reactivity patterns has been obtained by allowing appropriate metal fragments to react with elemental chalcogens or their derivatives. An important role is played by such compounds in the metal assisted synthesis of "chalcogenospecific" sulfur and selenium heterocycles[1] and Me_2C-substituted polysulfanes.[2] Moreover, they are of interest for applications ranging from the field of catalysis[3] to that of dry lubricants.[4] Also, it has recently been shown that organometallic chalcogenides may provide parent compounds for inorganic solid-state products under mild conditions.[5]

The chemistry of polysulfides[6-8] is reasonably well developed; several polyselenides[9-11] have also been reported. However, up to now the chemistry of tellurium in transition-metal compounds has received less attention. Some compounds containing a tellurium atom either at a vertex of a tetrahedral[12] or octahedral[13] frame or in a bridging position between two or three metal fragments have been described.[14] In the latter compounds, single or double tellurium to metal bonds are considered to exist according to the electronic requirements of the metal atoms. Only two examples of metal complexes containing tri-[15] or tetratellurium[16] moieties have been characterized, whereas a few transition-metal compounds containing the ditellurium unit have been described.[17-20] The Te_2 unit is generally linked to two or three metal fragments, one of which is always side-on bonded; the other fragments, when present, are either side-on[18] (I) or terminally[17,19] (II) bound. The geometric arrangements arising about Te_2 are as those illustrated in Chart I. Such arrangements point to a preference for side-on coordination and high connectivity by ditellurium in transition-metal compounds; the same propensity is exhibited by ditellurium in transition-metal carbonyl clusters.[21] The existence of stable monometal $LNiTe_2$ (III) compounds [L = 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos), bis(2-(diphenylphosphino)ethyl)phenylphosphane (p_3)],[20] which easily add $(ML)^{2+}$ to form type I compounds, confirms, on the one hand,

Chart I

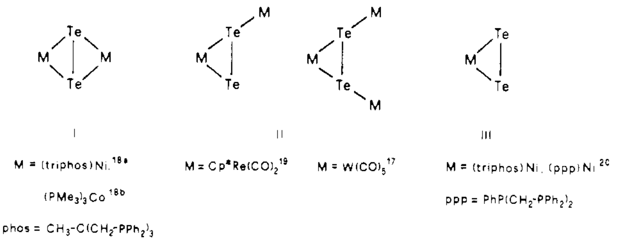

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Table I. Crystallographic Data for $[(np_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**1**), $[(pp_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**2**), and $[(pp_3)Rh]_2Te_2$ (**3**)

	1	2	3
formula	$C_{88}H_{92}N_2OP_6Rh_2Te_2$	$C_{88}H_{92}OP_8Rh_2Te_2$	$C_{84}H_{84}P_8Rh_2Te_2$
fw	1840.58	1874.51	1802.41
space group	$P2_1/n^a$	$P2_1/n^a$	$P\bar{1}$
a, Å	13.532 (4)	13.598 (9)	13.543 (2)
b, Å	19.669 (6)	20.243 (6)	13.716 (3)
c, Å	14.492 (9)	14.492 (5)	13.370 (4)
α, deg	90	90	111.65 (2)
β, deg	91.89 (7)	92.55 (4)	95.62 (2)
γ, deg	90	90	119.05 (2)
V, Å^3	3855 (3)	3985 (3)	1897 (1)
Z	2	2	1
λ(Mo Kα), Å	0.71069	0.71069	0.71069
d(calcd), g cm^{-3}	1.585	1.562	1.577
μ(Mo Kα), cm^{-1}	13.35	13.30	13.93
R^b	0.051	0.058	0.038
$R_w{}^c$	0.054	0.061	0.040

[a] Alternative setting of $P2_1/c$ (No. 14 of ref 27). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

the propensity of ditellurium for side-on coordination and high connectivity, but it also shows that a low connectivity is allowed by suitable metal fragments.

Tellurium-containing compounds have been obtained through routes involving the reaction of metal fragments with (i) the unstable H_2Te,[17,19] (ii) Zintl phases,[16] (iii) naked polycationic species,[15] or (iv) tellurium-releasing reagents.[5] We have found that a polytellurides solution, easily generated in situ, provides a useful system to give tellurium-rich compounds in the presence of cationic metal fragments.[18,20] On investigating the behavior of such a polytellurides solution toward rhodium–polyphosphane fragments, we have obtained the $[LRh]_2Te_2{\cdot}$THF [L = tris(2-(diphenylphosphino)ethyl)amine (np$_3$), tris(2-(diphenylphosphino)ethyl)phosphine (pp$_3$); THF = tetrahydrofuran] compounds. The pp$_3$ derivative crystallizes also without solvent. In these compounds the ditellurium unit is terminally bound to two rhodium–L systems. A short account of the results has already appeared.[22] While the manuscript was in preparation, the structure of a manganese dimer containing terminally bonded Te_2 has been reported.[5]

Experimental Section

General Data. All solvents were reagent grade and were appropriately dried and freed of molecular oxygen prior to use. All reactions were performed under a dry nitrogen atmosphere. All NMR spectra were collected on a Varian VXR 300 spectrometer (^{1}H at 299.9 MHz and ^{31}P at 121.4 MHz). Phosphorus-31 positive chemical shifts are to high frequency relative to an 85% H_3PO_4 external standard at 0.0 ppm. Analytical data for carbon, hydrogen, and nitrogen were obtained in the Microanalitical Laboratory of the Chemistry Department of the University of Florence with a Carlo Erba (Mod. 1106) elemental analyzer; phosphorus and tellurium elemental analyses were performed by Mikroanalytisches Labor Pascher, Remagen, FRG. The ligand tris(2-(diphenylphosphino)ethyl)amine (np$_3$)[23] and the complex $[RhCl(cod)]_2$[24] (cod = cycloocta-1,5-diene) were prepared according to published procedures. $AgBF_4$ and $(Bu_4N)BH_4$ were purchased from Fluka AG, tellurium powder was purchased from Merck, and the ligand tris(2-(diphenylphosphino)ethyl)phosphine (pp$_3$) was purchased from Pressure Chemical Co.; all of them were used without further purification. All compounds were collected on a sintered glass frit, in a closed system, and washed with ethanol and light petroleum (bp 40–70 °C) in turn before being dried under a stream of nitrogen.

Preparation of $[LRh]_2Te_2{\cdot}$THF [L = np$_3$ (1), pp$_3$ (2)]. $AgBF_4$ (1 mmol) was added to $[RhCl(cod)]_2$ (0.5 mmol) dissolved in acetone (40 mL); the resulting solution was stirred for 1 h at 40 °C and filtered to eliminate AgCl. The ligand (np$_3$ or pp$_3$) (1 mmol) in tetrahydrofuran (40 mL) was added to give a red solution. In a second vessel, solid $(Bu_4N)BH_4$ (1.9 mmol) was added to a suspension of tellurium (1 mmol) in tetrahydrofuran (30 mL), and the resulting slurry was stirred at 60 °C for 1 h. In the meantime, tellurium dissolved, yielding a deep purple solution, which was quickly added at room temperature to the rhodium–ligand solution. Deep brown crystals of the complexes were obtained by leaving the system at 0 °C overnight in the dark. Yield: 54% for **1** and 61% for **2**. Anal. Calcd (found) for $[(np_3)Rh]_2Te_2{\cdot}$THF, $C_{88}H_{92}N_2OP_6Rh_2Te_2$ (**1**): C, 57.43 (57.62); H, 5.04 (5.15); P, 10.10 (10.02); Te, 13.87 (13.71). Calcd (found) for $[(pp_3)Rh]_2Te_2{\cdot}$THF, $C_{88}H_{92}OP_8Rh_2Te_2$ (**2**): C, 56.39 (56.24); H, 4.95 (4.94); P, 13.22 (13.37); Te, 13.61 (13.84). For the pp$_3$ derivative, both solvated and unsolvated crystals were obtained in the same batch (see the X-ray Structural Determinations section). Since it was not possible to determine the relative amounts of the two forms (see the Results section), the calculated values listed above for **2** refer to the pure solvated form whereas the found values are for the mixture. ^{31}P{^{1}H} (CD_2Cl_2 solution) for $[(np_3)Rh]_2Te_2{\cdot}$THF (**1**): δ 29.68 ppm [d, ^1J(P–Rh) = 141.0 Hz]; δ 26.41 ppm [d, ^1J(P–Rh) = 144.4 Hz].

X-ray Structural Determinations. Crystals of the compounds are in the form of irregularly shaped prisms. Those of the np$_3$ derivative, containing tetrahydrofuran solvate molecules, belong to the monoclinic system. In the case of the pp$_3$ derivative, two sorts of crystals, indistinguishable on the basis of simple visual inspection, were found to be present in the same batch. There were tetrahydrofuran-containing crystals, isomorphous to those of the np$_3$ derivative, and triclinic crystals not containing solvate molecules. In addition to the structure of $[(np_3)Rh]_2Te_2{\cdot}$THF (**1**), those of both forms of the pp$_3$ derivative, $[(pp_3)Rh]_2Te_2{\cdot}$THF (**2**) and $[(pp_3)Rh]_2Te_2$ (**3**), were investigated in order to detect any possible conformational effects due to differences in packing and to the presence or absence of solvent in the lattice.

Crystal data for the three compounds are given in Table I. A CAD4 automated diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) were used for all operations. Unit-cell parameters were determined by least-squares refinement of the setting angles of 24 reflections having 22° ≤ 2θ ≤ 26° (**1**), 20° ≤ 2θ ≤ 28° (**2**), or 22° ≤ 2θ ≤ 26° (**3**). Intensity data were collected at room temperature by the ω–2θ scan technique. The intensities of three standard reflections, monitored periodically throughout data collection, showed a notable linear decrease (ca. 30%) for **1** and a smaller one (4%) for **3**, but showed only random fluctuations for **2**. The raw intensity data for **1** and **3** were properly rescaled to account for the decay. Data sets were corrected for absorption empirically once the structure had been solved.[25] Corrections for Lorentz and polarization effects were applied. The principal computer programs used in the crystallographic calculations are given in ref 26.

The structures of **1** and **3** were determined by combinations of direct methods and heavy-atom procedures. That of **2** was refined by using as initial atomic positions those from the structure of **1**. In the full-matrix least-squares refinements the function $\sum w(|F_o| - |F_c|)^2$ was minimized, with weights $w = [\sigma^2(F_o) + gF_o{}^2]^{-1}$, where g = 0.0002 (**1**), 0.0005 (**2**),

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Table II. Positional Parameters and Isotropic Thermal Parameters for $[(np_3)Rh]_2Te_2{\cdot}C_4H_8O^{a-c}$

atom	*x*	*y*	*z*	U_{eq}/U, Å^2
Rh	392 (1)	1544 (1)	818 (1)	25 (1)
Te	210 (1)	248 (1)	849 (1)	41 (1)
P(1)	17 (2)	1605 (1)	2362 (2)	33 (1)
P(2)	−931 (2)	1862 (1)	−146 (2)	31 (1)
P(3)	1983 (1)	1490 (1)	336 (2)	32 (1)
N	663 (4)	2639 (3)	932 (5)	34 (3)
C(1)	226 (8)	2932 (4)	1767 (7)	57 (6)
C(2)	352 (7)	2501 (4)	2624 (7)	45 (6)
C(3)	226 (8)	2995 (5)	108 (8)	61 (7)
C(4)	−826 (6)	2799 (4)	−96 (7)	45 (6)
C(5)	1726 (7)	2797 (4)	954 (8)	61 (7)
C(6)	2342 (6)	2398 (4)	320 (7)	43 (5)
C(11)	683 (6)	1171 (4)	3329 (6)	40 (6)
C(12)	1543 (6)	848 (5)	3171 (7)	51 (6)
C(13)	2112 (8)	587 (6)	3903 (8)	66 (8)
C(14)	1787 (10)	630 (7)	4779 (9)	89 (10)
C(15)	926 (11)	938 (9)	4933 (9)	128 (14)
C(16)	357 (9)	1210 (7)	4215 (8)	78 (9)
C(21)	−1250 (6)	1534 (4)	2714 (6)	34 (5)
C(22)	−1917 (6)	2062 (5)	2617 (7)	49 (6)
C(23)	−2920 (7)	1982 (6)	2836 (7)	60 (7)
C(24)	−3242 (7)	1386 (6)	3160 (8)	64 (8)
C(25)	−2618 (8)	845 (6)	3246 (8)	70 (8)
C(26)	−1618 (7)	911 (5)	3010 (8)	61 (7)
C(31)	−2210 (5)	1703 (4)	158 (6)	35 (5)
C(32)	−2440 (6)	1117 (5)	623 (7)	46 (6)
C(33)	−3413 (7)	954 (6)	815 (7)	60 (7)
C(34)	−4153 (7)	1404 (7)	569 (7)	68 (8)
C(35)	−3945 (7)	1984 (7)	129 (8)	75 (9)
C(36)	−2981 (6)	2144 (6)	−100 (7)	58 (7)
C(41)	−1033 (6)	1698 (4)	−1384 (6)	36 (5)
C(42)	−1684 (7)	1209 (5)	−1775 (7)	51 (6)
C(43)	−1707 (9)	1046 (6)	−2684 (8)	67 (8)
C(44)	−1085 (9)	1371 (7)	−3280 (8)	71 (9)
C(45)	−461 (9)	1850 (7)	−2940 (8)	73 (9)
C(46)	−421 (7)	2022 (5)	−2002 (8)	60 (8)
C(51)	2374 (6)	1228 (4)	−805 (6)	32 (5)
C(52)	1679 (6)	1105 (4)	−1497 (7)	45 (6)
C(53)	1957 (9)	952 (5)	−2394 (8)	68 (8)
C(54)	2947 (9)	911 (5)	−2596 (8)	63 (8)
C(55)	3646 (7)	1024 (5)	−1903 (8)	52 (7)
C(56)	3370 (6)	1172 (5)	−1026 (7)	45 (6)
C(61)	2933 (5)	1085 (4)	1062 (6)	36 (5)
C(62)	3394 (6)	1409 (5)	1796 (7)	51 (7)
C(63)	4049 (7)	1067 (6)	2376 (7)	65 (8)
C(64)	4241 (7)	382 (6)	2222 (8)	64 (8)
C(65)	3797 (7)	42 (6)	1499 (8)	63 (7)
C(66)	3137 (6)	403 (5)	923 (7)	47 (6)
C(71)[d]	5600	−200	4900	149 (6)
C(72)[d]	5080	−420	5570	149 (6)
C(73)[d]	4430	260	5490	149 (6)
C(74)[d]	4500	580	4540	149 (6)
C(75)[d]	5490	340	4390	149 (6)

[a] Coordinates are multiplied by 10^4 and temperature factors by 10^3. [b] In this and following tables standard deviations in the least significant digit(s) are given in parentheses. [c] The thermal parameter given for anisotropically refined atoms is the isotropic equivalent thermal parameter, defined as $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i{\cdot}\mathbf{a}_j$; the temperature factor for atoms refined isotropically is of the form $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$. [d] Positions from ΔF maps, used for the model of the solvate C_4H_8O molecule (see text); these were assigned 0.5 occupancy factor and an isotropic overall thermal parameter, and were not refined.

Table III. Positional Parameters and Isotropic Thermal Parameters for $[(pp_3)Rh]_2Te_2{\cdot}C_4H_8O^{a,b}$

atom	*x*	*y*	*z*	U_{eq}/U, Å^2
Rh	505 (1)	1576 (1)	634 (1)	41 (1)
Te	494 (1)	275 (1)	728 (1)	56 (1)
P(1)	179 (3)	1722 (2)	2189 (3)	55 (2)
P(2)	−874 (2)	1792 (2)	−320 (3)	47 (2)
P(3)	2112 (2)	1555 (2)	170 (3)	48 (2)
P(4)	698 (3)	2655 (2)	619 (3)	56 (2)
C(1)	282 (11)	3049 (8)	1661 (10)	74 (4)
C(2)	442 (12)	2608 (7)	2468 (9)	74 (4)
C(3)	−1 (10)	3031 (7)	−322 (10)	69 (4)
C(4)	−989 (10)	2705 (6)	−393 (10)	62 (4)
C(5)	1991 (10)	2916 (8)	523 (10)	74 (4)
C(6)	2526 (10)	2416 (7)	−41 (11)	69 (4)
C(11)	897 (5)	1344 (4)	3154 (4)	55 (3)
C(12)	1700 (5)	942 (4)	2982 (4)	66 (4)
C(13)	2288 (5)	694 (4)	3716 (4)	79 (4)
C(14)	2071 (5)	849 (4)	4623 (4)	92 (5)
C(15)	1267 (5)	1252 (4)	4795 (4)	128 (5)
C(16)	680 (5)	1499 (4)	4060 (4)	81 (4)
C(21)	−1076 (6)	1607 (5)	2571 (5)	77 (4)
C(22)	−1786 (6)	2081 (5)	2327 (5)	106 (4)
C(23)	−2762 (6)	1986 (5)	2553 (5)	145 (4)
C(24)	−3029 (6)	1417 (5)	3024 (5)	150 (5)
C(25)	−2320 (6)	943 (5)	3268 (5)	175 (5)
C(26)	−1344 (6)	1038 (5)	3042 (5)	107 (5)
C(31)	−2119 (4)	1555 (4)	−1 (5)	52 (3)
C(32)	−2239 (4)	993 (4)	540 (5)	61 (4)
C(33)	−3181 (4)	793 (4)	765 (5)	60 (4)
C(34)	−4002 (4)	1155 (4)	449 (5)	85 (4)
C(35)	−3882 (4)	1716 (4)	−92 (5)	100 (5)
C(36)	−2940 (4)	1916 (4)	−318 (5)	92 (5)
C(41)	−937 (5)	1583 (4)	−1563 (5)	54 (4)
C(42)	−1633 (5)	1145 (4)	−1949 (5)	71 (4)
C(43)	−1630 (5)	993 (4)	−2887 (5)	87 (4)
C(44)	−933 (5)	1279 (4)	−3440 (5)	99 (5)
C(45)	−237 (5)	1717 (4)	−3055 (5)	96 (5)
C(46)	−240 (5)	1869 (4)	−2116 (5)	82 (4)
C(51)	2491 (5)	1188 (4)	−908 (5)	52 (4)
C(52)	1775 (5)	969 (4)	−1557 (5)	65 (4)
C(53)	2051 (5)	736 (4)	−2413 (5)	86 (4)
C(54)	3043 (5)	721 (4)	−2621 (5)	81 (4)
C(55)	3759 (5)	940 (4)	−1972 (5)	74 (4)
C(56)	3483 (5)	1173 (4)	−1116 (5)	63 (4)
C(61)	3053 (5)	1205 (4)	961 (5)	49 (4)
C(62)	3533 (5)	1588 (4)	1642 (5)	78 (4)
C(63)	4184 (5)	1292 (4)	2289 (5)	95 (5)
C(64)	4353 (5)	613 (4)	2255 (5)	80 (4)
C(65)	3873 (5)	230 (4)	1574 (5)	77 (4)
C(66)	3222 (5)	526 (4)	927 (5)	61 (4)
C(71)[c]	5291 (15)	343 (9)	5891 (15)	126 (3)
C(72)[c]	4344 (15)	359 (9)	5437 (15)	126 (3)
C(73)[c]	4472 (15)	363 (9)	4470 (15)	126 (3)
C(74)[c]	5498 (15)	349 (9)	4326 (15)	126 (3)
C(75)[c]	6004 (15)	337 (9)	5204 (15)	126 (3)

[a] Coordinates are multiplied by 10^4 and temperature factors by 10^3. [b] The isotropic and equivalent isotropic thermal parameters are defined as in Table II. [c] Atoms of the model for the C_4H_8O solvate molecule, which was refined as a rigid group with idealized geometry, 0.5 occupancy factor, and an overall thermal parameter.

or 0.0005 (**3**). In the final cycles, all atoms were refined anisotropically, except for H atoms, which were assigned isotropic temperature factors ca. 20% larger than the equivalent isotropic temperature factors of the corresponding C atoms, and for atoms of the tetrahydrofuran solvate molecule in **1** and **2**, which were assigned overall *U* values. In the case of the structure of **2**, for which less observed reflections were available than for **1** or **3** due to poorer quality data, phenyl groups were refined as rigid bodies with idealized geometry. Hydrogen atoms in all structures were introduced in calculated positions, with C–H = 1.00 Å. The position of the tetrahydrofuran molecule in **1** and **2**, lying in proximity to an inversion center, was found to be affected by disorder. In the case of **1**, attempts to refine a model for the solvent consisting of a pentagonal rigid group failed, due to large oscillations. Finally, the C scattering factor and 0.5 population parameter were assigned to five sites in an approximate pentagonal arrangement, chosen among ten maxima shown by ΔF maps in the solvate molecule region, and such positions were not refined. On the other hand, in the case of **2**, refinements could be performed on a pentagonal rigid group of C atoms with 0.5 occupancy factors; this procedure was then adopted in the final refinement for **2** as it also produced a significant lowering of *R*. In no case were attempts to assign the O atom position in the solvent model made; neither were H atoms included in that model. Small damping factors were used in the final refinement cycles for **2** and **3**. The final *R* values appear in Table I. Scattering factors for the neutral atoms and the anomalous dispersion corrections for Rh and Te were taken from ref 28.

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(27) *International Tables for Crystallography*; Reidel: Dordrecht, The Netherlands, 1983; Vol. A, p 224.

Table IV. Positional Parameters and Equivalent Isotropic Thermal Parameters for $[(pp_3)Rh]_2Te_2$[a,b]

atom	x	y	z	U_{eq}, Å^2
Te	−285 (1)	853 (1)	534 (1)	59 (1)
Rh	813 (1)	2194 (1)	2844 (1)	45 (1)
P(1)	1006 (2)	3934 (2)	2786 (2)	55 (1)
P(2)	2542 (2)	2205 (2)	3132 (2)	53 (1)
P(3)	−824 (2)	778 (2)	3119 (2)	56 (1)
P(4)	1474 (2)	3372 (2)	4711 (2)	58 (1)
C(1)	1869 (6)	4977 (6)	5150 (5)	67 (2)
C(2)	1073 (6)	4933 (6)	4208 (5)	73 (2)
C(3)	2833 (5)	3572 (6)	5416 (5)	64 (2)
C(4)	3549 (5)	3543 (6)	4600 (5)	64 (2)
C(5)	377 (6)	2736 (6)	5371 (5)	75 (2)
C(6)	−388 (6)	1293 (6)	4672 (5)	75 (2)
C(11)	−207 (5)	3807 (6)	1883 (5)	64 (2)
C(12)	−1374 (5)	2795 (6)	1581 (6)	79 (2)
C(13)	−2342 (6)	2629 (7)	912 (6)	100 (2)
C(14)	−2162 (6)	3472 (7)	518 (7)	103 (2)
C(15)	−1006 (6)	4491 (7)	816 (7)	107 (2)
C(16)	−44 (6)	4667 (6)	1501 (6)	90 (2)
C(21)	2308 (5)	5066 (5)	2571 (6)	68 (2)
C(22)	2403 (6)	4688 (6)	1489 (6)	85 (2)
C(23)	3365 (6)	5476 (7)	1273 (7)	113 (2)
C(24)	4226 (7)	6671 (7)	2119 (8)	144 (2)
C(25)	4175 (7)	7086 (7)	3182 (8)	128 (2)
C(26)	3219 (6)	6279 (6)	3422 (7)	98 (2)
C(31)	3579 (5)	2615 (5)	2338 (5)	58 (2)
C(32)	4684 (5)	2810 (6)	2622 (6)	75 (2)
C(33)	5444 (6)	3131 (7)	2000 (6)	86 (2)
C(34)	5103 (6)	3300 (6)	1129 (6)	90 (2)
C(35)	4016 (6)	3112 (7)	827 (6)	107 (2)
C(36)	3227 (6)	2753 (6)	1409 (6)	81 (2)
C(41)	2597 (5)	905 (5)	3185 (5)	60 (2)
C(42)	2298 (6)	−104 (6)	2177 (6)	77 (2)
C(43)	2274 (6)	−1131 (7)	−2174 (7)	94 (2)
C(44)	2613 (6)	−1120 (7)	3175 (7)	107 (2)
C(45)	2969 (7)	−102 (7)	4160 (7)	114 (2)
C(46)	2942 (6)	895 (6)	4190 (6)	97 (2)
C(51)	−1373 (5)	−895 (5)	2549 (5)	62 (2)
C(52)	−2432 (5)	−1774 (6)	2613 (6)	76 (2)
C(53)	−2792 (6)	−3011 (6)	2226 (6)	85 (2)
C(54)	−2079 (6)	−3388 (6)	1794 (6)	92 (2)
C(55)	−1048 (6)	−2541 (6)	1721 (7)	95 (2)
C(56)	−703 (5)	−1305 (6)	2072 (6)	72 (2)
C(61)	−2270 (5)	597 (5)	2765 (5)	60 (2)
C(62)	−3019 (5)	−120 (6)	1629 (5)	67 (2)
C(63)	−4101 (6)	−246 (6)	1323 (6)	82 (2)
C(64)	−4437 (6)	356 (7)	2141 (7)	100 (2)
C(65)	−3700 (6)	1077 (7)	3248 (7)	101 (2)
C(66)	−2623 (6)	1213 (6)	3564 (6)	81 (2)

[a] Coordinates are multiplied by 10^4 and temperature factors by 10^3. [b] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$.

Table V. Selected Bond Distances (Å) for $[(np_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**1**), $[(pp_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**2**), and $[(pp_3)Rh]_2Te_2$ (**3**)[a,b]

	1	**2**	**3**
Te–Te′	2.691 (1)	2.691 (2)	2.760 (1)
Rh–Te	2.562 (1)	2.638 (1)	2.718 (1)
Rh–P(1)	2.314 (2)	2.334 (4)	2.304 (2)
Rh–P(2)	2.319 (2)	2.321 (4)	2.328 (2)
Rh–P(3)	2.288 (2)	2.315 (3)	2.308 (2)
Rh–E	2.190 (6)	2.200 (4)	2.196 (2)

[a] Te′ is related to Te through an inversion center. [b] Key: E = N (**1**), P (**2**, **3**).

Table VI. Selected Bond Angles (deg) for $[(np_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**1**), $[(pp_3)Rh]_2Te_2{\cdot}C_4H_8O$ (**2**), and $[(pp_3)Rh]_2Te_2$ (**3**)[a,b]

	1	**2**	**3**
Rh–Te–Te′	111.2 (1)	112.1 (1)	113.2 (1)
Te–Rh–P(1)	90.5 (1)	94.3 (1)	88.6 (1)
Te–Rh–P(2)	101.9 (1)	102.2 (1)	104.2 (1)
Te–Rh–P(3)	92.9 (1)	90.3 (1)	92.1 (1)
Te–Rh–E	173.3 (2)	173.2 (1)	169.9 (1)
P(1)–Rh–P(2)	112.3 (1)	111.6 (2)	116.9 (1)
P(1)–Rh–P(3)	122.4 (1)	120.4 (2)	122.2 (1)
P(2)–Rh–P(3)	123.0 (1)	125.3 (2)	118.7 (1)
E–Rh–P(1)	85.3 (2)	85.0 (2)	85.0 (1)
E–Rh–P(2)	84.5 (2)	84.3 (2)	85.7 (1)
E–Rh–P(3)	85.0 (2)	84.3 (2)	84.8 (1)

[a] Te′ is related to Te through an inversion center. [b] Key: E = N (**1**), P (**2**, **3**).

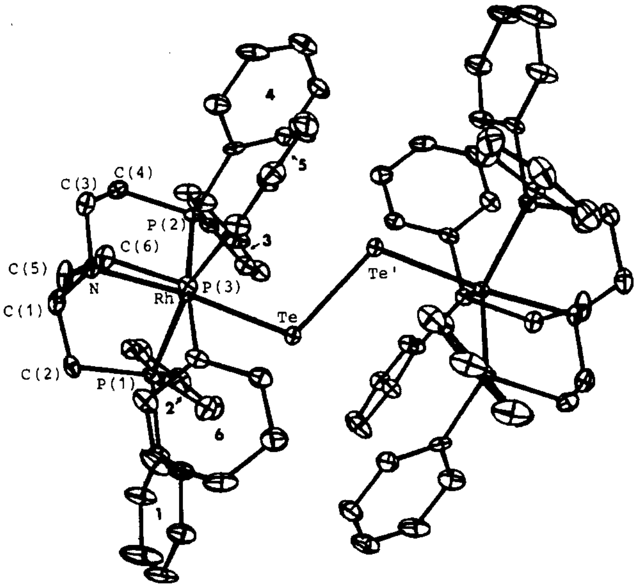

Figure 1. Perspective view of the centrosymmetric $[(np_3)Rh]_2Te_2$ molecule in **1**, with 20% probability ellipsoids. Only symmetry-independent atoms are labeled, except Te′, which is related to Te through an inversion center. Phenyl groups are numbered, but carbon atoms are not labeled for clarity.

Tables II–IV contain lists of atomic positional parameters and isotropic or equivalent isotropic thermal parameters for **1**–**3**. Values of selected bond distances and angles for the three compounds appear in Tables V and VI. Available as supplementary material are details on data collections and structure refinements, lists of anisotropic thermal parameters for the three compounds, extended tables of bond distances and angles, lists of hydrogen atom coordinates, and tables of observed and calculated structure factors. See paragraph at end of paper regarding supplementary material.

Results and Discussion

Synthesis and Properties of $[LRh]_2Te_2{\cdot}THF$ [L = np_3 (1), pp_3 (2)]. The method developed for the synthesis of the $[LRh]_2Te_2{\cdot}THF$ [L = np_3 (**1**), pp_3 (**2**)] compounds involves the direct reaction of a polytellurides solution with cationic rhodium–ligand fragments generated as already described.[29] The wine red polytellurides solution is prepared by reaction of gray tellurium with 2 equiv of $(Bu_4N)BH_4$ in THF at 55–60 °C (heating is necessary to accomplish the reduction). Although the reduction of selenium by boron hydrides had already been used to generate polyanions,[30] an analogous procedure had not been considered for tellurium. Reduction of tellurium in organic solvents (THF, CH_3CN) had been previously accomplished by electrochemical processes induced by ultrasound.[31] Compounds **1** and **2** are obtained as analytically pure deep brown crystals in good yield. They are mildly air and moisture sensitive, and are sparingly soluble in dichloromethane. The solutions are unstable even under nitrogen, decomposition to [LRhCl][32] occurring in a short time at room temperature. The

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(28) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 71, 148.

(29) Di Vaira, M.; Stoppioni, P.; Peruzzini, M. *J. Organomet. Chem.* **1987**, *333*, C53.

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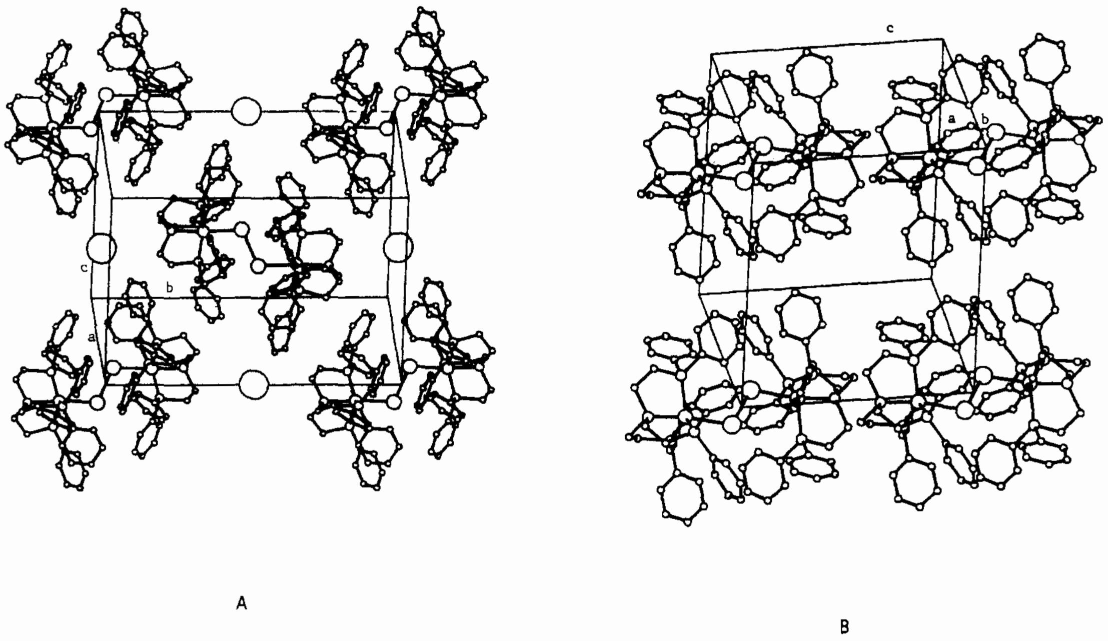

Figure 2. Views of the crystal packing for the two forms of the pp_3 derivative: (A) solvated, compound **2**; (B) unsolvated, compound **3**. Large circles denote the positions of disordered solvent molecules, in proximity to inversion centers.

pp_3 derivative crystallizes also without solvent (see the X-ray Structural Determinations section), crystals of the two forms being present in the same batch. Their relative amounts cannot be safely evaluated from elemental analysis data as the calculated values for the two forms are very close. Attempts to obtain such an estimate were undertaken by running the ^1H NMR spectrum of the solvated and unsolvated mixture in CD_2Cl_2. Tetrahydrofuran signals appear sharp and exhibit the expected shifts; on the other hand, the signals due to the pp_3 ligand are broad and significantly shifted both with respect to those of the free ligand and to those of pp_3 in diamagnetic metal complexes.[32] Such an effect, probably caused by paramagnetic species formed by decomposition upon dissolution, prevented the accurate integration of the ^1H signal and the evaluation of the relative amounts of the two forms.

Structures of the Compounds. The structure of each of the compounds **1**–**3** consists of discrete, dimeric [{(L)Rh}Te$_2${Rh(L)}] molecules [L = np_3 (**1**), pp_3 (**2**, **3**)]. In the structures of the isomorphous compounds **1** and **2**, there are in addition tetrahydrofuran molecules from the solvent, lying in proximity to an inversion center, in a disordered arrangement. In the $[LRh]_2Te_2$ dimeric molecule (Figure 1) the Rh–Te–Te–Rh zigzag fragment is present, with the Te_2 unit end-on coordinated to the metal atoms. An inversion center lies in the middle of the Te–Te bond, in each structure, so that only half of the dimeric molecule is symmetry independent. Each metal atom is coordinated by one Te atom, by the three equatorial P atoms of the tripod L ligand, and by the axial (N or P) atom of the same ligand, in a slightly distorted trigonal-bipyramidal environment. The overall molecular conformation is closely similar for the three compounds, notable differences involving only the "soft" Rh–Te and Te–Te bonds (Table V). In particular, the Rh–Te distance increases steadily on going from compound **1** to **3**. The Te–Te distance, on the other hand, is constant for **1** and **2** [2.691 (2) Å] but increases significantly [2.760 (1) Å] in compound **3**. All of these Te–Te bond lengths are shorter than that existing in elemental Te, 2.835 (2) Å;[33] the value found for compound **3** is close to that [2.7628 (7) Å] reported for the manganese dimer in ref 5. Remarkably, there are overall larger differences in such bond lengths between compounds **2** and **3**, formed by the same pp_3 ligand, than between **1**, formed by np_3, and **2**. The expansion of the Rh–Te–Te–Rh core, forming the softest part of the compounds, in **3** may be due to the different packing with respect to the other two compounds.

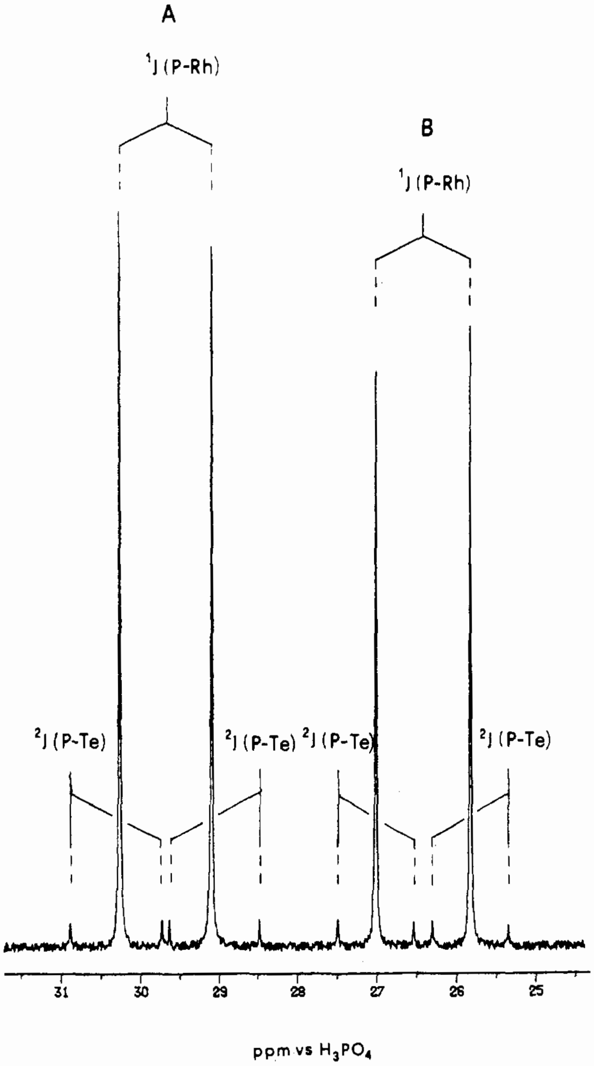

Figure 3. $^{31}P\{^1H\}$ spectrum of **1** in CD_2Cl_2: (A) δ = 29.68 ppm, ^1J(P–Rh) = 141.0 Hz, ^2J(P–Te) = 152 Hz; (B) δ = 26.41 ppm, ^1J(P–Rh) = 144.4 Hz, ^2J(P–Te) = 116 Hz.

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(32) (a) Di Vaira, M.; Peruzzini, M.; Zanobini, F.; Stoppioni, P. *Inorg. Chim. Acta* **1983**, *69*, 37. (b) Bianchini, C.; Masi, D.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 6411.

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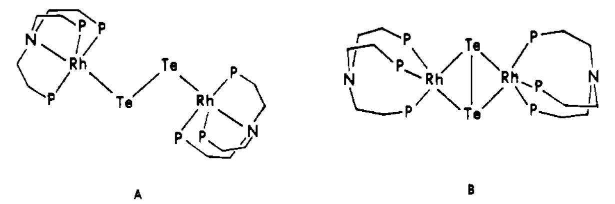
Chart II



Packing diagrams for **2** and **3** are shown in Figure 2.

Behavior of the Compounds in Solution. In order to obtain $^{31}P\{^1H\}$ NMR spectra of the compounds, **1** and **2** were dissolved in CD_2Cl_2. However, **2** decomposes to [$(pp_3)RhCl$] before any signal can be detected. The $^{31}P\{^1H\}$ NMR spectrum of **1** (Figure 3) consists of two doublets [29.68 ppm, 141.0 Hz (A) and 26.41 ppm, 144.4 Hz (B), with 1.3:1 intensity ratio] having similar chemical shifts and coupling constants, which are in the usual range for tripodal polyphosphane-rhodium complexes.[32b] The two doublets present satellites whose intensities are consistent with coupling of the P atoms to tellurium (^{125}Te, $I = {}^1/_2$, 7% natural abundance). The coupling constants [$^2J(P-Te) = 152.0$ (A) and 116.0 Hz (B)] are 1 order of magnitude smaller than the $^1J(P-Te)$ coupling in compounds containing tellurium directly bonded to phosphorus.[34] A similar decrease in coupling constants, from $^1J(Te-H) = 151$ Hz to $^2J(Te-H) = 16$ Hz, has been found in a rhenium hydrotelluride hydride complex.[19] Satellites due to ^{125}Te have been recently reported for the $^{31}P\{^1H\}$ NMR spectra of the [$Cp(Et_3P)(CO)Fe]_2Te_n$ ($n = 1, 2$) compounds and their $^2J(P-Te)$ coupling constants agree with the present ones.[35]

Although the poor solubility of the compound prevented us from running variable-temperature $^{31}P\{^1H\}$ spectra, some considerations are nevertheless possible. The pattern shown in Figure 3 is inconsistent with the solid-state structure of **1**, which requires six equivalent phosphorus atoms in view of the possibility of rotations about the Rh-Te and Te-Te bonds in solution.[36] Also, inequivalent phosphorus atoms on the same np_3 ligand would produce an AB_2X or ABCX spin system, at variance with the features observed for the spectrum. Furthermore, the observed intensity ratio of the two doublets (1.3:1) rules out any inequivalence between the two sets of P atoms belonging to different np_3 ligands in the same molecule. The features of the spectrum may be accounted for by the presence of two species in solution, having different geometries. Possible arrangements are as shown in Chart II, where A corresponds to the structure of compound **1** in the solid state and B may be considered as arising from A through an isomerization reaction that involves the detachment of the apical nitrogen donor of the np_3 ligand. The possibility of such rearrangements is supported by the following considerations: (i) isomerization processes have been observed for compounds where two metal fragments are bound to X_2 (X = Se,[37] Te[19]) units and consist of a shift of one metal-ligand unit from terminal to side on[37] or vice versa;[19] (ii) a side-on-bridging Te_2 unit between two P_3Rh fragments has been found in the structure of the compound [$(triphos)Rh]_2Te_2$ containing a tripodal tridentate ligand;[22] (iii) the detachment of the nitrogen atom of the np_3 ligand, required for the A → B conversion, should easily occur in presence of a predominantly soft set of donor atoms,[38] such as that existing in the present compounds; (iv) the proposed geometry for species B is not in contrast to the stereochemical nonrigidity assumed above as nonrigidity has been observed for the compounds containing a Te_2 group side-on bonded to two $M-L_3$ fragments, which have been described up to now.[18]

Conclusions. Rhodium compounds containing the end-on-coordinated ditellurium unit are synthesized from easily accessible reagents and easy manipulation. The Rh-Te-Te-Rh zigzag skeleton is highly reactive, suggesting that such compounds could behave as sources of tellurium fragments for the synthesis of new tellurium-containing compounds. The Te-Te distances in the present compounds are typical of Te-Te single bonds in Te_2 dimetal derivatives. A difference in such bond lengths of 0.07 Å between compounds **2** and **3** is essentially due to different packing in the solid. This reveals how sensitive the Te-Te distance may be to various factors. This feature, combined with the documented possibility of octet expansion on Te,[39] adds interest to the chemistry of heavy main-group elements such as Te.

Registry No. **1**, 123726-12-5; **2**, 123726-14-7; **3**, 123726-13-6; [$RhCl(cod)]_2$, 12092-47-6; Te, 13494-80-9; $(Bu_4N)BH_4$, 33725-74-5.

Supplementary Material Available: Full details of the crystal data and crystallographic data collections (Table SI), thermal parameters for **1-3** (Tables SII-SIV), bond distances (Tables SV-SVII) and angles (Tables SVIII-SX) for **1-3**, and hydrogen atom coordinates (Tables SXI-SXIII) for **1-3** (23 pages); listings of observed and calculated structure factors (58 pages). Ordering information is given on any current masthead page.

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Oxidation Chemistry of Ruthenium-Salen Complexes

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The synthesis of [$Ru^{III}(salen)(X)(Y)]^n$ [$n = -1$, $(X)(Y) = (CN)_2$; $n = 0$, $(X)(Y) = (PPh_3)(PBu_3)$, $(PPh_3)(py)$; $n = 1$, $(X)(Y) = (PPh_3)(N_3)$, $(PPh_3)(TsO)$ (TsO = tosylate anion)] from [$Ru^{III}(salen)(PPh_3)(Cl)$] is described. These ruthenium(III) complexes are dark green air-stable solids. Their cyclic voltammograms display reversible Ru(IV)/Ru(III) and Ru(III)/Ru(II) couples with $E°$ ranging from 0.37 to 0.76 V and -0.47 to -1.06 V vs $Ag/AgNO_3$ (0.1 M), respectively. At room temperature, they catalyze oxidation of alkenes by PhIO. With norbornene and cyclooctene, epoxides are formed. For arenes, oxidative cleavage of C═C bond is the major reaction pathway. The mechanism of the catalytic oxidation is discussed.

Introduction

The use of metal-salen [salen = *N,N'*-ethylenebis(salicyideneaminato) anion] complexes to catalyze oxidation of hydrocarbons by oxygen atom donors has been receiving much attention in recent years. This area is highlighted by the works of Kochi and co-workers on the oxidation chemistry of salen complexes of chromium,[1] manganese,[2] and nickel.[3] The isolation of the reactive [$Cr^V(salen)O]^{+}$ [1a] by these workers indicates that the pathways

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