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Synthesis and Characterization of the New Clusters $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$, $Ru_3(CO)_6(PPh_3)_3(\mu_3\text{-}Te)_2$, $Ru_4(CO)_{10}(PPh_3)(\mu_4\text{-}Te)_2$, and $Ru_4(CO)_9(\mu\text{-}Ph_2PCH_2PPh_2)(\mu_4\text{-}Te)_2$

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The compound $Ru_4(CO)_{11}(\mu_4\text{-}Te)_2$ (**1**) has been prepared by refluxing a benzene solution containing $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$. The compounds $Ru_3(CO)_6(PPh_3)_3(\mu_3\text{-}Te)_2$ (**2**) and $Ru_4(CO)_{10}(PPh_3)(\mu_4\text{-}Te)_2$ (**3**) were obtained from the room-temperature reaction of **1** with PPh_3. Similarly, $Ru_4(CO)_9(\mu\text{-}Ph_2PCH_2PPh_2)(\mu_4\text{-}Te)_2$ (**4**) was obtained from the reaction of **1** with $Ph_2PCH_2PPh_2$ at room temperature. The structure of **1–4** were established by single-crystal X-ray diffraction analysis. Crystal data: **1**, orthorhombic, *Pccn*, $a = 6.924$ (2) Å, $b = 16.289$ (6) Å, $c = 18.054$ (6) Å, $V = 2036$ (1) Å^3, $Z = 4$, $R(F) = 4.16\%$; **2**, monoclinic, $P2_1/n$, $a = 10.539$ (4) Å, $b = 27.39$ (1) Å, $c = 20.415$ (7) Å, $\beta = 94.96$ (3)°, $V = 5870$ (4) Å^3, $Z = 4$, $R(F) = 4.96\%$; **3**, orthorhombic, *Pbca*, $a = 19.070$ (5) Å, $b = 18.157$ (4) Å, $c = 19.272$ (5) Å, $V = 6673$ (3) Å^3, $Z = 8$, $R(F) = 3.65\%$; **4**, triclinic, $P\bar{1}$, $a = 13.255$ (3) Å, $b = 17.610$ (5) Å, $c = 19.189$ (5) Å, $\alpha = 65.39$ (2)°, $\beta = 78.25$ (2)°, $\gamma = 84.13$ (2)°, $V = 3986$ (2) Å^3, $Z = 4$, $R(F) = 2.97\%$.

Introduction

In recent years the chemistry of transition-metal, non-metal cluster compounds has undergone rapid developments; the activity has been particularly high for metal–chalcogen clusters.[1,2] The incorporation of main-group elements into transition-metal carbonyl clusters introduces novel structural and reactivity features. Single-atom, main-group-element ligands are being increasingly used as bridges between different metal fragments in cluster growth reactions. The main-group elements often have a key role in stabilizing the bonding network in the transition-metal, non-metal clusters. Consequently, these clusters often have the ability to add or remove ligands or electrons while retaining the cluster integrity.

The triply bridging sulfido ligand has been extensively used for the purpose of cluster growth and stabilization purposes.[2,3] In particular, the numerous sulfidoosmium carbonyl clusters obtained systematically by stepwise addition of metal carbonyl units to the μ_3-S ligands demonstrate the importance of this type of ligand. The much larger tellurium has also been used as a bridge between different metal fragments in cluster synthesis, but indications are that the tellurium-containing clusters will be structurally and chemically different from those containing sulfur.[4,5] In contrast to the S and Se analogues, $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ reacts with a variety of Lewis bases (L) to form adducts to the form $(CO)_6Fe_2(\mu_3\text{-}Te)_2Fe(CO)_3L$.[6] We have shown that the $Fe(CO)_3L$ fragment in the adduct is susceptible to replacement by "$M(PPh_3)_2$" (M = Ni, Pd, Pt) units to form the mixed-metal complexes $(CO)_6Fe_2(\mu_3\text{-}Te)_2M(PPh_3)_2$.[7] Such transmetalation reactions should provide a simple route to mixed-metal cluster compounds.

In this paper, we describe the preparation of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ and its reactivity toward triphenylphosphine and bis(diphenylphosphino)methane. These compounds are believed to be the first examples or ruthenium clusters with bridging tellurium ligands to be structurally characterized.

Experimental Section

All manipulations were carried out under an atmosphere of pure argon with use of standard Schlenk techniques. Solvents were purified, dried, and distilled under argon prior to use. $Fe_3Te_2(CO)_9$ was prepared by an established procedure.[6] Infrared spectra were recorded on a Nicolet 5DXB FTIR spectrometer as solutions in dichloromethane in NaCl cells.

Preparation of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (1). A mixture of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ (0.1 g, 0.148 mmol) and $Ru_3(CO)_{12}$ (0.189 g, 0.295 mmol) in 90 mL of benzene solvent was refluxed for 6 h. The solvent was removed in vacuo, and the brown residue was chromatographed on a silica gel column. Elution with hexane separated trace amounts of unreacted $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$. Further elution with a 75:25 mixture of hexane and dichloromethane gave the red product, $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (yield 0.023 g, 8%, based on the amount of $Ru_3(CO)_{12}$ consumed). IR (CH_2Cl_2; ν(CO), cm^{-1}): 2087 (w), 2044 (s), 2026 (m), 1989 (m), and 1827 (w).

Reaction of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ with Triphenylphosphine. Triphenylphosphine (380 mg, 1.45 mmol) was added to 80 mL of a CH_2Cl_2 solution of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (100 mg, 0.104 mmol). The solution was stirred at room temperature for 12 h. Removal of the solvent and chromatography of the residue on silica gel TLC plates using a 70:30 mixture of hexane and dichloromethane separated the following products: yellow-brown $Ru_4(CO)_8(\mu\text{-}CO)_2(PPh_3)(\mu_4\text{-}Te)_2$ (**3**) (yield 0.002 g, 3%) (IR (CH_2Cl_2; ν(CO), cm^{-1}): 2062 (w), 2025 (s), 1997 (w), 1973 (w, sh), 1856 (w), and 1825 (w)); pink $Ru_3(CO)_6(PPh_3)_3(\mu_3\text{-}Te)_2$ (**2**) (yield 0.028 g, 21%) (IR (CH_2Cl_2; ν(CO), cm^{-1}): 2027 (sh), 1987 (s), 1957 (s), and 1943 (sh)).

Reaction of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ with Bis(diphenylphosphino)methane (dppm). A mixture of $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (190 mg, 0.196 mmol) and dppm (100 mg, 0.260 mmol) dissolved in 75 mL of dichloromethane was stirred at room temperature for 10 h. Removal of the solvent and chromatography of the residue on silica gel column with a 65:35 mixture of hexane and dichloromethane gave a single yellow band of $Ru_4(CO)_8(\mu\text{-}CO)(\mu\text{-}dppm)(\mu_4\text{-}Te)_2$ (**4**) (yield 0.032 g, 32%). IR (CH_2Cl_2; ν(CO), cm^{-1}): 2040 (m), 2009 (s), 1964 (m), and 1790 (w).

Crystal Structure Determinations for 1–4. Crystallographic data are collected in Table I. Suitable crystals were obtained from methylene chloride/hexane mixtures and mounted on glass fibers. For **1–3** systematic absences in the diffraction data uniquely determined the space group. For **4**, the centrosymmetric alternative was initially assumed and later verified by the chemically reasonable results of refinement. All data sets were empirically corrected for absorption and *Lp* effects.

The structures were solved by direct methods and completed by subsequent difference Fourier syntheses. The asymmetric unit for **1** consists of a half-molecule on a 2-fold axis passing through O(2), C(2), and the midpoints of the Ru(1)–Ru(1a), Ru(2)–Ru(2a), and Te···Te vectors. Two crystallographically independent, but chemically similar, molecules

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Table I. Crystallographic Data for **1–4**

	1	**2**	**3**	**4**
formula	$Ru_4Te_2(CO)_{11}$	$C_{60}H_{45}O_6P_3Ru_3Te_2$	$C_{28}H_{15}O_{10}PRu_4Te_2$	$C_{34}H_{22}O_9Ru_4Te_4$
fw	967.58	1513.27	1201.84	1295.93
space group	*Pccn*	*P*2$_1$/*n*	*Pbca*	*P*1̄
a, Å	6.924 (2)	10.539 (4)	19.070 (5)	13.255 (3)
b, Å	16.389 (6)	27.39 (1)	18.157 (4)	17.610 (5)
c, Å	18.054 (6)	20.415 (7)	19.272 (5)	19.189 (5)
α, deg				65.39 (2)
β, deg		94.96 (3)		78.25 (2)
γ, deg				84.13 (2)
V, Å^3	2036 (1)	5870 (4)	6673 (3)	3986 (2)
Z	4	4	8	4
D(calc), g/cm^3	3.157	1.716	2.394	2.162
μ(Mo Kα), cm^{-1}	58.16	20.99	24.71	30.72
temp, °C	23	23	23	23
T(max)/*T*(min)	1.55	1.10	1.71	1.25
radition (λ, Å)	Mo Kα (0.71073)			
R(*F*),	4.16	4.96	3.65	2.97
$R_w(F)$,	4.48	5.24	3.94	3.21

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for **1**

Te	*x*	*y*	*z*	U^a
Te	75.5 (6)	7079.8 (3)	2647.4 (3)	28.2 (2)
Ru(1)	1739.8 (9)	8298.4 (3)	3493.1 (3)	30.8 (2)
Ru(2)	1708.2 (8)	8338.9 (3)	1900.9 (3)	26.9 (2)
O(1)	3685 (12)	9739 (4)	4235 (5)	80 (3)
O(2)	2500	7500	4977 (6)	88 (5)
O(3)	−2020 (10)	8785 (5)	4204 (5)	82 (3)
O(4)	260 (18)	9940 (7)	2508 (5)	87 (4)
O(5)	4205 (11)	9188 (5)	754 (4)	74 (3)
O(6)	−1503 (13)	8282 (6)	765 (6)	111 (5)
C(1)	2938 (13)	9187 (5)	3950 (5)	44 (3)
C(2)	2500	7500	4319 (7)	48 (4)
C(3)	−629 (13)	8615 (6)	3935 (5)	48 (3)
C(4)	898 (15)	9304 (5)	2413 (5)	46 (3)
C(5)	3281 (12)	8880 (5)	1185 (5)	43 (3)
C(6)	−336 (14)	8313 (6)	1192 (6)	57 (3)

[a] Equivalent isotropic *U* defined as one–third of the trace of the orthogonalized U_{ij} tensor.

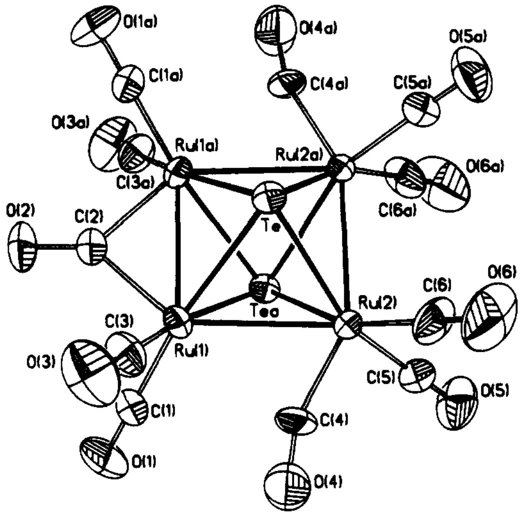


Figure 1. Molecular structure of **1**. A crystallographic 2-fold axis contains C(2), O(2), and the midpoints of Ru(1)–Ru(1a), Ru(2)–Ru(2a), and Te⋯Te(a) vectors. In this and the following figures, the ellipsoids are drawn at the 40% probability level and hydrogen atoms have been deleted.

of **4** constitute its asymmetric unit.

The phenyl rings of **2–4** were constrained to rigid, planar hexagons. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogen atoms were treated as idealized isotropic contributions.

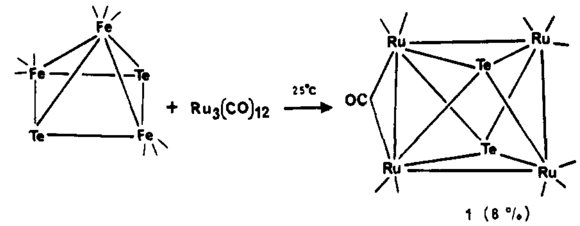
All computations used the SHELXTL (5.1) program library (G. Sheldrick, Nicolet Corp., Madison, WI). Tables II, IV, VI, and VIII give the atomic coordinates, and Tables III, VII, and IX, the bond distances and angles for **1–4**, respectively.

Table III. Bond Distances and Angles for **1**

(a) Bond Distances (Å)			
Te–Ru(1)	2.758 (1)	Te–Ru(2)	2.702 (1)
Te–Ru(1A)	2.753 (1)	Te–Ru(2A)	2.691 (1)
Ru(1)–Ru(2)	2.877 (1)	Ru(1)–C(1)	1.861 (9)
Ru(1)–C(2)	2.046 (9)	Ru(1)–C(3)	1.895 (9)
Ru(1)–Te(A)	2.753 (1)	Ru(1)–Ru(1A)	2.806 (1)
Ru(2)–C(4)	1.909 (9)	Ru(2)–C(5)	1.907 (9)
Ru(2)–C(6)	1.908 (10)	Ru(2)–Te(A)	2.691 (1)
Ru(2)–Ru(2A)	2.945 (1)	O(1)–C(1)	1.157 (12)
O(2)–C(2)	1.188 (16)	O(3)–C(3)	1.113 (12)
O(4)–C(4)	1.139 (14)	O(5)–C(5)	1.125 (12)
O(6)–C(6)	1.119 (14)		
(b) Bond Angles (deg)			
Ru(1)–Te–Ru(2)	63.6 (1)	Ru(1)–Te–Ru(1A)	61.2 (1)
Ru(2)–Te–Ru(1A)	96.4 (1)	Ru(1)–Te–Ru(2A)	96.6 (1)
Ru(2)–Te–Ru(2A)	66.2 (1)	Ru(1A)–Te–Ru(2A)	63.8 (1)
Te–Ru(1)–Ru(2)	57.3 (1)	Te–Ru(1)–C(1)	172.6 (3)
Ru(2)–Ru(1)–C(1)	115.3 (3)	Te–Ru(1)–C(2)	93.1 (2)
Ru(2)–Ru(1)–C(2)	138.1 (2)	C(1)–Ru(1)–C(2)	93.3 (3)
Te–Ru(1)–C(3)	93.9 (3)	Ru(2)–Ru(1)–C(3)	114.0 (3)
C(1)–Ru(1)–C(3)	89.3 (4)	C(2)–Ru(1)–C(3)	95.2 (3)
Te–Ru(1)–Te(A)	82.3 (1)	Ru(2)–Ru(1)–Te(A)	57.0 (1)
C(1)–Ru(1)–Te(A)	93.6 (3)	C(2)–Ru(1)–Te(A)	93.2 (2)
C(3)–Ru(1)–Te(A)	171.0 (3)	Te–Ru(1)–Ru(1A)	59.3 (1)
Ru(2)–Ru(1)–Ru(1A)	91.4 (1)	C(1)–Ru(1)–Ru(1A)	123.6 (3)
C(2)–Ru(1)–Ru(1A)	46.7 (2)	C(3)–Ru(1)–Ru(1A)	125.3 (3)
Te(A)–Ru(1)–Ru(1A)	59.5 (1)	Te–Ru(2)–Ru(1)	59.1 (1)
Te–Ru(2)–C(4)	105.1 (3)	Ru(1)–Ru(2)–C(4)	62.4 (3)
Te–Ru(2)–C(5)	158.2 (2)	Ru(1)–Ru(2)–C(5)	133.2 (3)
C(4)–Ru(2)–C(5)	96.6 (4)	Te–Ru(2)–C(6)	90.4 (3)
Ru(1)–Ru(2)–C(6)	132.5 (3)	C(4)–Ru(2)–C(6)	97.2 (4)
C(5)–Ru(2)–C(6)	88.8 (4)	Te–Ru(2)–Te(A)	84.5 (1)
Ru(1)–Ru(2)–Te(A)	59.2 (1)	C(4)–Ru(2)–Te(A)	102.1 (3)
C(5)–Ru(2)–Te(A)	89.1 (3)	C(6)–Ru(2)–Te(A)	160.7 (3)
Te–Ru(2)–Ru(2A)	56.7 (1)	Ru(1)–Ru(2)–Ru(2A)	88.6 (1)
C(4)–Ru(2)–Ru(2A)	150.9 (3)	C(5)–Ru(2)–Ru(2A)	102.5 (2)
C(6)–Ru(2)–Ru(2A)	104.8 (3)	Te(A)–Ru(2)–Ru(2A)	57.1 (1)
Ru(1)–C(1)–O(1)	180.0 (12)	Ru(1)–C(2)–O(2)	136.7 (2)
Ru(1)–C(2)–Ru(1A)	86.6 (5)	O(2)–C(2)–Ru(1A)	136.7 (2)
Ru(1)–C(3)–O(3)	178.3 (9)	Ru(2)–C(4)–O(4)	159.4 (9)
Ru(2)–C(5)–O(5)	178.7 (7)	Ru(2)–C(6)–O(6)	178.0 (9)

Results

The tetraruthenium cluster $Ru_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}Te)_2$ (**1**) was prepared by refluxing a mixture of $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$ in benzene solvent for 6 h (eq 1). Compound **1** was



(1)

1 (8 %)

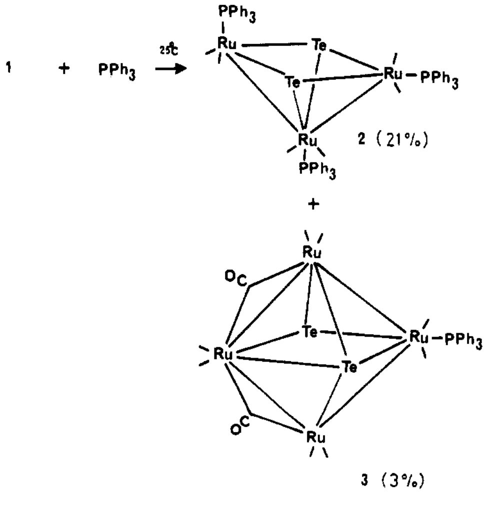
Table IV. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **2**

	x	*y*	*z*	U^a		*x*	*y*	*z*	U^a
Te(1)	10624.4 (6)	1641.6 (2)	2253.9 (3)	42.4 (2)	C(46)	7434	629	26	46 (3)
Te(2)	7559.6 (6)	1844.5 (2)	1557.2 (3)	41.4 (2)	C(51)	4862 (6)	886 (2)	471 (2)	50 (3)
Ru(1)	8373.5 (7)	1492.9 (3)	2757.4 (3)	34.9 (2)	C(52)	3644	1060	557	66 (4)
Ru(2)	9050.9 (7)	1062.1 (3)	1511.6 (3)	42.4 (3)	C(53)	3276	1136	1189	72 (5)
Ru(3)	9193.7 (8)	2442.0 (3)	2237.7 (3)	42.6 (3)	C(54)	4128	1040	1735	83 (5)
P(1)	9345 (2)	1407 (1)	3832 (1)	39.7 (8)	C(55)	5347	866	1649	65 (4)
P(2)	7369 (2)	599 (1)	931 (1)	45.5 (9)	C(56)	5714	789	1017	44 (3)
P(3)	9931 (3)	2941 (1)	1424 (1)	51.2 (9)	C(61)	6263 (6)	−307 (3)	1241 (3)	69 (5)
C(1)	7979 (10)	817 (4)	2763 (4)	50 (3)	C(62)	6282	−809	1356	95 (6)
C(2)	6855 (10)	1751 (4)	3001 (5)	58 (4)	C(63)	7406	−1072	1318	110 (7)
C(3)	10009 (11)	499 (4)	1848 (5)	65 (4)	C(64)	8511	−833	1165	102 (6)
C(4)	9881 (10)	1143 (5)	757 (5)	71 (5)	C(65)	8492	−331	1049	71 (5)
C(5)	7775 (10)	2813 (4)	2432 (5)	63 (4)	C(66)	7368	−68	1087	60 (4)
C(6)	10356 (10)	2735 (4)	2908 (5)	61 (4)	C(71)	8667 (8)	3706 (3)	688 (3)	66 (4)
C(11)	12034 (7)	1465 (2)	3974 (3)	59 (4)	C(72)	8051	4157	621	73 (5)
C(12)	13248	1300	3863	72 (5)	C(73)	7849	4432	1178	105 (6)
C(13)	13411	831	3617	72 (5)	C(74)	8263	4256	1802	111 (7)
C(14)	12358	527	3483	71 (5)	C(75)	8879	3806	1869	86 (6)
C(15)	11143	692	3594	57 (4)	C(76)	9081	3531	1312	60 (4)
C(16)	10981	1161	3840	45 (3)	C(81)	11949 (8)	3625 (3)	1468 (4)	111 (7)
C(21)	9088 (6)	2390 (2)	4220 (2)	59 (4)	C(82)	13194	3782	1637	132 (8)
C(22)	9213	2777	4665	83 (5)	C(83)	14094	3458	1930	99 (7)
C(23)	9765	2700	5302	68 (5)	C(84)	13749	2977	2054	94 (6)
C(24)	10193	2235	5494	66 (4)	C(85)	12505	2820	1885	77 (5)
C(25)	10068	1848	5049	55 (4)	C(86)	11605	3144	1592	58 (4)
C(26)	9516	1925	4412	44 (3)	C(91)	8637 (5)	2566 (3)	288 (3)	57 (4)
C(31)	7190 (6)	1013 (2)	4331 (3)	67 (4)	C(92)	8510	2382	−352	68 (4)
C(32)	6518	725	4746	73 (5)	C(93)	9584	2321	−697	99 (6)
C(33)	7169	401	5182	68 (4)	C(94)	10786	2445	−404	112 (7)
C(34)	8492	365	5203	74 (5)	C(95)	10913	2629	236	86 (5)
C(35)	9164	652	4788	60 (4)	C(96)	9838	2690	582	53 (4)
C(36)	8513	976	4351	47 (3)	O(1)	7710 (8)	418 (3)	2848 (3)	77 (3)
C(41)	7527 (7)	1084 (2)	−272 (3)	59 (4)	O(2)	5866 (7)	1913 (3)	3129 (4)	81 (3)
C(42)	7551	1116	−953	67 (4)	O(3)	10610 (10)	193 (4)	2077 (4)	103 (4)
C(43)	7482	693	−1335	82 (5)	O(4)	10471 (7)	1203 (4)	315 (4)	115 (5)
C(44)	7389	238	−1037	83 (5)	O(5)	6883 (8)	3026 (3)	2576 (5)	103 (4)
C(45)	7365	206	−356	66 (4)	O(6)	11044 (9)	2893 (4)	3303 (4)	101 (4)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthognalized $\mathbf{U}_{ij}$ tensor.

characterized by infrared spectroscopy and mass spectrometry. The mass spectrum showed the parent ion at *m/e* 972 and peaks corresponding to the successive loss of 11 carbonyl groups. The infrared spectrum of **1** in the carbonyl region shows bands at 2087 (w), 2044 (s), 2026 (m), 1989 (m), and 1827 (w) cm^{-1}, indicating the presence of terminal and bridging carbonyl ligands. Dark red, air-stable crystals of **1** were obtained by slow evaporation of a CH_2Cl_2/hexane solution, and an X-ray analysis was undertaken. An ORTEP drawing of the molecular structure of **1** is shown in Figure 1. Interatomic bond distances and angles are listed in Table III. The cluster consists of a trapezoidal arrangement of four ruthenium atoms that is bridged on each face by a μ_4-Te ligand and along the Ru(1)–Ru(1a) edge by a μ-CO ligand. It is structurally very similar to the recently reported $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}S)_2$.[3] The shortest metal–metal bond in **1** contains a bridging carbonyl ligand, Ru(1)–Ru(1a) = 2.806 (1) Å. In $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}S)_2$ also the shortest Fe–Fe bond is bridged by a carbonyl group. The edges unbridged by μ-CO are longer: Ru(1)–Ru(2) = 2.877 (1) Å, and Ru(2)–Ru(2a) = 2.945 (1) Å. In both $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu_4\text{-}S)_2$ and **1**, the equal edges of the trapezoid contain semibridging carbonyl ligands, but the semibridging effect is slightly stronger in the iron cluster than in our ruthenium cluster: Ru(2)–C(4)–O(4a) = 159.4 (9)°, and Fe–C–O = 161.2 (8)°. Cluster **1** can also be compared with $Ru_4(CO)_9(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$, the structure of which was determined in the form of the bis(phosphine)-substituted derivative, $Ru_4(CO)_7(PMe_2Ph)_2(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$.[8] The sulfido cluster differs from **1** in containing two bridging carbonyl ligands but is similar to **1** with respect to the Ru–Ru bonds; in both compounds the two Ru–Ru bonds associated with the carbonyl ligands are significantly shorter than the unbridged Ru–Ru bonds.

Room-temperature stirring of **1** with PPh_3 in dichloromethane solvent formed a pink compound (**2**) as the major product of the reaction and a yellow-brown compound (**3**) in low yield (eq 2).



(2)

The infrared spectrum of **2** shows bands at 2027 (sh), 1987 (s), 1957 (s), and 1943 (sh) cm^{-1}, indicating the presence of only terminally bonded carbonyls. Dark brown crystals of **2** were obtained by slow evaporation of solvent from solutions in a dichloromethane/hexane solvent mixture, and an X-ray analysis was undertaken. An ORTEP diagram of the molecular structure of **2** is shown in Figure 2. Interatomic bond distances and angles are given in Table V. The molecule consists of a square-pyramidal arrangement of three ruthenium and two tellurium atoms. The two tellurium atoms and two of the ruthenium atoms form approximately a square base to the pyramid, Te(1)–Ru(2) = 2.670

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(8) Adams, R. D.; Babin, J. E.; Tasi, M. *Inorg. Chem.* **1986**, *25*, 4514.

Table V. Selected Bond Distances and Angles for **2**

(a) Bond Distances (Å)			
Te(1)–Ru(1)	2.697 (1)	Te(1)–Ru(2)	2.670 (1)
Te(1)–Ru(3)	2.659 (1)	Te(2)–Ru(1)	2.702 (1)
Te(2)–Ru(2)	2.664 (1)	Te(2)–Ru(3)	2.676 (1)
Ru(1)–Ru(2)	2.947 (1)	Ru(1)–Ru(3)	2.965 (1)
Ru(1)–P(1)	2.352 (2)	Ru(1)–C(1)	1.896 (10)
Ru(1)–C(2)	1.857 (11)	Ru(2)–P(2)	2.407 (3)
Ru(2)–C(3)	1.936 (12)	Ru(2)–C(4)	1.849 (10)
Ru(3)–P(3)	2.336 (3)	Ru(3)–C(5)	1.879 (11)
Ru(3)–C(6)	1.930 (10)	C(2)–O(2)	1.181 (13)
C(1)–O(1)	1.147 (12)	C(4)–O(4)	1.151 (13)
C(3)–O(3)	1.129 (15)	C(6)–O(6)	1.123 (13)
C(5)–O(5)	1.165 (14)		
(b) Bond Angles (deg)			
Ru(1)–Te(1)–Ru(2)	66.6 (1)	Ru(1)–Te(1)–Ru(3)	67.2 (1)
Ru(2)–Te(1)–Ru(3)	99.2 (1)	Ru(1)–Te(2)–Ru(2)	66.6 (1)
Ru(1)–Te(2)–Ru(3)	66.9 (1)	Ru(2)–Te(2)–Ru(3)	98.9 (1)
Te(1)–Ru(1)–Te(2)	79.7 (1)	Te(1)–Ru(1)–Ru(2)	56.3 (1)
Te(2)–Ru(1)–Ru(2)	56.1 (1)	Te(1)–Ru(1)–Ru(3)	55.8 (1)
Te(2)–Ru(1)–Ru(3)	56.1 (1)	Ru(2)–Ru(1)–Ru(3)	86.7 (1)
Te(1)–Ru(1)–P(1)	92.5 (1)	Te(2)–Ru(1)–P(1)	163.8 (1)
Ru(2)–Ru(1)–P(1)	130.3 (1)	Ru(3)–Ru(1)–P(1)	107.8 (1)
Te(1)–Ru(1)–C(1)	110.5 (3)	Te(2)–Ru(1)–C(1)	107.5 (2)
Ru(2)–Ru(1)–C(1)	71.6 (3)	Ru(3)–Ru(1)–C(1)	158.2 (3)
P(1)–Ru(1)–C(1)	88.5 (2)	Te(1)–Ru(1)–C(2)	148.4 (3)
Te(2)–Ru(1)–C(2)	83.9 (3)	Ru(2)–Ru(1)–C(2)	131.5 (3)
Ru(3)–Ru(1)–C(2)	92.7 (3)	P(1)–Ru(1)–C(2)	95.9 (3)
C(1)–Ru(1)–C(2)	100.1 (5)	Te(1)–Ru(2)–Te(2)	80.9 (1)
Te(1)–Ru(2)–Ru(1)	57.1 (1)	Te(2)–Ru(2)–Ru(1)	57.3 (1)
Te(1)–Ru(2)–P(2)	170.9 (1)	Te(2)–Ru(2)–P(2)	91.7 (1)
Ru(1)–Ru(2)–P(2)	114.4 (1)	Te(1)–Ru(2)–C(3)	89.6 (3)
Te(2)–Ru(2)–C(3)	156.8 (3)	Ru(1)–Ru(2)–C(3)	99.8 (3)
P(2)–Ru(2)–C(3)	95.4 (3)	Te(1)–Ru(2)–C(4)	95.0 (3)
Te(2)–Ru(2)–C(4)	104.8 (4)	Ru(1)–Ru(2)–C(4)	147.0 (4)
P(2)–Ru(2)–C(4)	91.9 (3)	C(3)–Ru(2)–C(4)	97.0 (5)
Te(1)–Ru(3)–Te(2)	80.9 (1)	Te(1)–Ru(3)–Ru(1)	57.0 (1)
Te(2)–Ru(3)–Ru(1)	57.0 (1)	Te(1)–Ru(3)–P(3)	105.6 (1)
Te(2)–Ru(3)–P(3)	103.2 (1)	Ru(1)–Ru(3)–P(3)	153.3 (1)
Te(1)–Ru(3)–C(5)	154.7 (3)	Te(2)–Ru(3)–C(5)	87.3 (3)
Ru(1)–Ru(3)–C(5)	97.9 (3)	P(3)–Ru(3)–C(5)	98.8 (3)
Te(1)–Ru(3)–C(6)	90.6 (3)	Te(2)–Ru(3)–C(6)	164.3 (3)
Ru(1)–Ru(3)–C(1)	71.6 (3)	Ru(3)–Ru(1)–C(1)	158.2 (3)
P(1)–Ru(1)–C(1)	88.5 (2)	Te(1)–Ru(1)–C(2)	148.4 (3)
Te(2)–Ru(1)–C(2)	83.9 (3)	Ru(2)–Ru(1)–C(2)	131.5 (3)
Ru(3)–Ru(1)–C(2)	92.7 (3)	P(1)–Ru(1)–C(2)	95.9 (3)
C(1)–Ru(1)–C(2)	100.1 (5)	Te(1)–Ru(2)–Te(2)	80.9 (1)
Te(1)–Ru(2)–Ru(1)	57.1 (1)	Te(2)–Ru(2)–Ru(1)	57.3 (1)
Te(1)–Ru(2)–P(2)	170.9 (1)	Te(2)–Ru(2)–P(2)	91.7 (1)
Ru(1)–Ru(2)–P(2)	114.4 (1)	Te(1)–Ru(2)–C(3)	89.6 (3)
Te(2)–Ru(2)–C(3)	156.8 (3)	Ru(1)–Ru(2)–C(3)	99.8 (3)
P(2)–Ru(2)–C(3)	95.4 (3)	Te(1)–Ru(2)–C(4)	95.0 (3)
Te(2)–Ru(2)–C(4)	104.8 (4)	Ru(1)–Ru(2)–C(4)	147.0 (4)
P(2)–Ru(2)–C(4)	91.9 (3)	C(3)–Ru(2)–C(4)	97.0 (5)
Te(1)–Ru(3)–Te(2)	80.9 (1)	Te(1)–Ru(3)–Ru(1)	57.0 (1)
Te(2)–Ru(3)–Ru(1)	57.0 (1)	Te(1)–Ru(3)–P(3)	105.6 (1)
Te(2)–Ru(3)–P(3)	103.2 (1)	Ru(1)–Ru(3)–P(3)	153.3 (1)
Te(1)–Ru(3)–C(5)	154.7 (3)	Te(2)–Ru(3)–C(5)	87.3 (3)
Ru(1)–Ru(3)–C(5)	97.9 (3)	P(3)–Ru(3)–C(5)	98.8 (3)
Te(1)–Ru(3)–C(6)	90.6 (3)	Te(2)–Ru(3)–C(6)	164.3 (3)
Ru(1)–Ru(3)–C(6)	107.3 (3)	P(3)–Ru(3)–C(6)	91.7 (3)
C(5)–Ru(3)–C(6)	95.4 (5)	Ru(1)–C(1)–O(1)	171.4 (7)
Ru(1)–C(2)–O(2)	177.0 (8)	Ru(2)–C(3)–O(3)	175.1 (10)
Ru(2)–C(4)–O(4)	175.2 (9)	Ru(3)–C(5)–O(5)	176.5 (10)
Ru(3)–C(6)–O(6)	178.0 (11)		

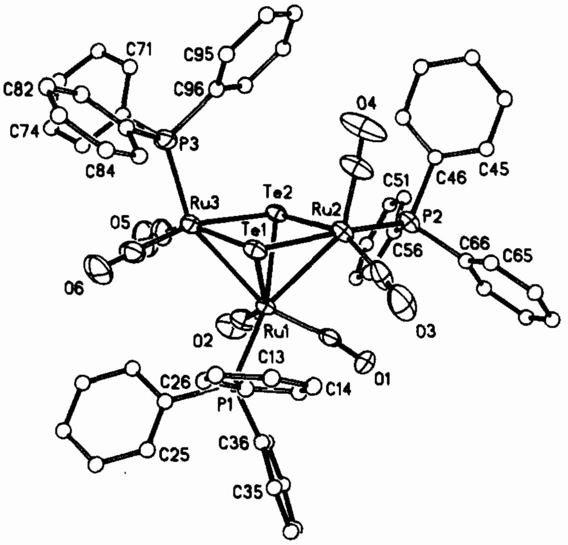

Figure 2. Molecular structure of **2**. The carbon atoms of the phenyl rings are drawn as arbitrary radius spheres.

Table VI. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **3**

	x	*y*	*z*	U^a
Te(1)	7807.5 (3)	957.9 (3)	3398.8 (3)	45.4 (2)
Te(2)	7490.1 (3)	1905.4 (3)	1773.7 (3)	43.0 (2)
Ru(1)	8203.8 (4)	611.1 (4)	2038.5 (4)	44.8 (2)
Ru(2)	8585.8 (4)	1943.1 (4)	2681.3 (4)	48.1 (2)
Ru(3)	6797.7 (4)	772.3 (4)	2427.8 (4)	46.6 (2)
Ru(4)	7113.0 (3)	2218.7 (3)	3094.5 (3)	36.1 (2)
P	6907 (1)	2469 (1)	4270 (1)	40 (1)
O(1)	8512 (4)	355 (4)	526 (3)	88 (3)
O(2)	9058 (5)	−715 (4)	2414 (4)	95 (3)
O(3)	9738 (4)	1208 (5)	1873 (4)	84 (3)
O(4)	7141 (4)	−553 (4)	1564 (4)	73 (3)
O(5)	9609 (4)	2042 (5)	3861 (4)	104 (4)
O(6)	9158 (5)	3398 (4)	2180 (5)	93 (4)
O(7)	5513 (5)	794 (5)	1532 (5)	118 (4)
O(8)	5997 (5)	−249 (4)	3352 (4)	105 (4)
O(9)	7537 (4)	3811 (4)	3004 (4)	74 (3)
O(10)	5636 (3)	2483 (4)	2607 (3)	70 (2)
C(1)	8405 (5)	445 (4)	1099 (5)	52 (3)
C(2)	8731 (5)	−207 (5)	2279 (4)	56 (3)
C(3)	9197 (5)	1310 (5)	2119 (5)	60 (3)
C(4)	7260 (5)	−23 (5)	1883 (4)	52 (3)
C(5)	9120 (5)	2014 (6)	3430 (6)	71 (4)
C(6)	8935 (5)	2842 (5)	2363 (6)	66 (4)
C(7)	5996 (6)	808 (6)	1868 (6)	74 (4)
C(8)	6306 (5)	136 (5)	3009 (5)	70 (4)
C(9)	7390 (5)	3198 (4)	3028 (5)	53 (3)
C(10)	6188 (4)	2356 (4)	2815 (4)	50 (3)
C(11)	8216 (3)	2971 (3)	4683 (3)	61 (4)
C(12)	8859	2923	5026	67 (4)
C(13)	9002	2319	5451	66 (4)
C(14)	8503	1764	5533	65 (4)
C(15)	7861	1812	5190	52 (3)
C(16)	7717	2415	4765	41 (3)
C(21)	6835 (4)	3893 (4)	4891 (4)	75 (5)
C(22)	6523	4580	4994	84 (6)
C(23)	5911	4764	4637	77 (5)
C(24)	5610	4261	4178	84 (6)
C(25)	5922	3574	4075	67 (5)
C(26)	6534	3390	4432	48 (4)
C(31)	6188 (3)	2037 (3)	5452 (3)	57 (3)
C(32)	5719	1604	5830	59 (3)
C(33)	5363	1028	5506	61 (4)
C(34)	5474	885	4804	60 (4)
C(35)	5943	1317	4425	48 (3)
C(36)	6299	1893	4749	41 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(1) Å, Te(1)–Ru(3) = 2.659 (1) Å, Te(2)–Ru(2) = 2.664 (1) Å, and Te(2)–Ru(3) = 2.676 (1) Å. The tellurium–ruthenium apical bonds, Te(1)–Ru(1) = 2.697 (1) Å and Te(2)–Ru(1) = 2.702 (1) Å, are slightly longer than the tellurium–ruthenium basal bonds. The average metal–metal bond distance in **2**, 2.956 (1) Å, is slightly greater than the average metal–metal bond distance in **1**, 2.876 (1) Å, and in $Ru_3(CO)_{12}$, 2.854 (1) Å,[9] but is similar to the average Ru–Ru bond distance in $\{Fe_2(CO)_6\}(\mu_4\text{-Te})(\mu_3\text{-Te})\{Ru_3(CO)_{11}\}$, 2.950 (1) Å.[6] Each metal atom contains two terminal carbonyl ligands and one triphenylphosphine ligand.

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(9) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* **1977**, *16*, 2655.

Table VII. Selected Distances and Angles for 3

(a) Bond Distances (Å)

Te(2)-Ru(1)	2.800 (1)	Te(1)-Ru(2)	2.705 (1)	Ru(3)-Ru(4)	2.985 (1)	Ru(3)-C(4)	1.992 (9)
Te(1)-Ru(3)	2.706 (1)	Te(1)-Ru(4)	2.709 (1)	Ru(3)-C(7)	1.872 (11)	Ru(3)-C(8)	1.862 (10)
Te(2)-Ru(1)	2.763 (1)	Te(2)-Ru(2)	2.726 (1)	Ru(4)-P	2.343 (2)	Ru(4)-C(9)	1.859 (8)
Te(2)-Ru(3)	2.751 (1)	Te(2)-Ru(4)	2.706 (1)	Ru(4)-C(10)	1.861 (9)	O(2)-C(2)	1.144 (12)
Ru(1)-Ru(2)	2.813 (1)	Ru(1)-Ru(3)	2.800 (1)	O(1)-C(1)	1.134 (11)	O(4)-C(4)	1.164 (11)
Ru(1)-C(1)	1.876 (9)	Ru(1)-C(2)	1.853 (9)	O(3)-C(3)	1.151 (12)	O(6)-C(6)	1.152 (13)
Ru(1)-C(3)	2.286 (9)	Ru(1)-C(4)	2.158 (9)	O(5)-C(5)	1.129 (13)	O(8)-C(8)	1.129 (13)
Ru(2)-Ru(4)	2.962 (1)	Ru(2)-C(3)	1.964 (9)	O(7)-C(7)	1.126 (15)	O(10)-C(10)	1.150 (11)
Ru(2)-C(5)	1.875 (10)	Ru(2)-C(6)	1.866 (10)	O(9)-C(9)	1.150 (11)		

(b) Bond Angles (deg)

Ru(1)-Te(1)-Ru(2)	61.4 (1)	Ru(1)-Te(1)-Ru(3)	61.1 (1)	C(5)-Ru(2)-C(6)	88.1 (5)	Te(1)-Ru(3)-Te(2)	83.2 (1)
Ru(2)-Te(1)-Ru(3)	96.9 (1)	Ru(1)-Te(1)-Ru(4)	96.9 (1)	Te(1)-Ru(3)-Ru(1)	61.1 (1)	Te(2)-Ru(3)-Ru(1)	59.7 (1)
Ru(2)-Te(1)-Ru(4)	66.3 (1)	Ru(3)-Te(1)-Ru(4)	66.9 (1)	Te(1)-Ru(3)-Ru(4)	56.6 (1)	Te(2)-Ru(3)-Ru(4)	56.1 (1)
Ru(1)-Te(2)-Ru(2)	61.7 (1)	Ru(1)-Te(2)-Ru(3)	61.0 (1)	Ru(1)-Ru(3)-Ru(4)	90.8 (1)	Te(1)-Ru(3)-C(4)	98.1 (3)
Ru(2)-Te(2)-Ru(3)	95.3 (1)	Ru(1)-Te(2)-Ru(4)	97.8 (1)	Te(2)-Ru(3)-C(4)	95.1 (3)	Ru(1)-Ru(3)-C(4)	50.1 (3)
Ru(2)-Te(2)-Ru(4)	66.1 (1)	Ru(3)-Te(2)-Ru(4)	66.3 (1)	Ru(4)-Ru(3)-C(4)	140.9 (3)	Te(1)-Ru(3)-C(7)	167.2 (3)
Te(1)-Ru(1)-Te(2)	81.3 (1)	Te(1)-Ru(1)-Ru(2)	57.6 (1)	Te(2)-Ru(3)-C(7)	95.8 (3)	Ru(1)-Ru(3)-C(7)	129.1 (4)
Te(2)-Ru(1)-Ru(2)	58.5 (1)	Te(1)-Ru(1)-Ru(3)	57.8 (1)	Ru(4)-Ru(3)-C(7)	112.5 (3)	C(4)-Ru(3)-C(7)	94.7 (4)
Te(2)-Ru(1)-Ru(3)	59.3 (1)	Ru(2)-Ru(1)-Ru(3)	92.3 (1)	Te(1)-Ru(3)-C(8)	91.1 (3)	Te(2)-Ru(3)-C(8)	168.9 (3)
Te(1)-Ru(1)-C(1)	174.5 (3)	Te(2)-Ru(1)-C(1)	93.4 (3)	Ru(1)-Ru(3)-C(8)	125.4 (3)	Ru(4)-Ru(3)-C(8)	112.8 (3)
Ru(2)-Ru(1)-C(1)	120.7 (3)	Ru(3)-Ru(1)-C(1)	118.2 (3)	C(4)-Ru(3)-C(8)	95.2 (4)	C(7)-Ru(3)-C(8)	87.6 (5)
Te(1)-Ru(1)-C(2)	95.3 (3)	Te(2)-Ru(1)-C(2)	174.5 (3)	Te(1)-Ru(4)-Te(2)	84.0 (1)	Te(1)-Ru(4)-Ru(2)	56.8 (1)
Ru(2)-Ru(1)-C(2)	116.0 (3)	Ru(3)-Ru(1)-C(2)	122.4 (3)	Te(2)-Ru(4)-Ru(2)	57.3 (1)	Te(1)-Ru(4)-Ru(3)	56.5 (1)
C(1)-Ru(1)-C(2)	90.1 (4)	Te(1)-Ru(1)-C(3)	92.0 (2)	Te(2)-Ru(4)-Ru(3)	57.6 (1)	Ru(2)-Ru(4)-Ru(3)	85.8 (1)
Te(2)-Ru(1)-C(3)	87.1 (2)	Ru(2)-Ru(1)-C(3)	43.8 (2)	Te(1)-Ru(4)-P	92.1 (1)	Te(2)-Ru(4)-P	174.1 (1)
Ru(3)-Ru(1)-C(3)	135.9 (2)	C(1)-Ru(1)-C(3)	89.2 (4)	Ru(2)-Ru(4)-P	116.9 (1)	Ru(3)-Ru(4)-P	123.6 (1)
C(2)-Ru(1)-C(3)	88.7 (4)	Te(1)-Ru(1)-C(4)	91.4 (2)	Te(1)-Ru(4)-C(9)	133.2 (3)	Te(2)-Ru(4)-C(9)	93.5 (3)
Te(2)-Ru(1)-C(4)	91.0 (2)	Ru(2)-Ru(1)-C(4)	137.4 (2)	Ru(2)-Ru(4)-C(9)	82.7 (3)	Ru(3)-Ru(4)-C(9)	15.3 (3)
Ru(3)-Ru(1)-C(4)	45.1 (2)	C(1)-Ru(1)-C(4)	87.2 (4)	P-Ru(4)-C(9)	85.9 (3)	Te(1)-Ru(4)-C(10)	129.7 (2)
C(2)-Ru(1)-C(4)	93.4 (4)	C(3)-Ru(1)-C(4)	175.7 (3)	Te(2)-Ru(4)-C(10)	90.5 (3)	Ru(2)-Ru(4)-C(10)	147.5 (3)
Te(1)-Ru(2)-Te(2)	83.7 (1)	Te(1)-Ru(2)-Ru(1)	61.0 (1)	Ru(3)-Ru(4)-C(10)	78.6 (3)	P-Ru(4)-C(10)	95.4 (3)
Te(2)-Ru(2)-Ru(1)	59.8 (1)	Te(1)-Ru(2)-Ru(4)	56.9 (1)	C(9)-Ru(4)-C(10)	97.0 (4)	Ru(1)-C(1)-O(1)	178.2 (8)
Te(2)-Ru(2)-Ru(4)	56.6 (1)	Ru(1)-Ru(2)-Ru(4)	91.0 (1)	Ru(1)-C(2)-O(2)	178.6 (8)	Ru(1)-C(3)-Ru(2)	82.5 (3)
Te(1)-Ru(2)-C(3)	102.7 (3)	Te(2)-Ru(2)-C(3)	95.0 (3)	Ru(1)-C(3)-O(3)	128.7 (8)	Ru(2)-C(3)-O(3)	148.7 (8)
Ru(1)-Ru(2)-C(3)	53.7 (3)	Ru(4)-Ru(2)-C(3)	144.1 (3)	Ru(1)-C(4)-Ru(3)	84.8 (3)	Ru(1)-C(4)-O(4)	132.6 (7)
Te(1)-Ru(2)-C(5)	90.0 (5)	Te(2)-Ru(2)-C(5)	169.2 (3)	Ru(3)-C(4)-O(4)	142.4 (8)	Ru(2)-C(5)-O(5)	176.8 (9)
Ru(1)-Ru(2)-C(5)	124.2 (3)	Ru(4)-Ru(2)-C(5)	112.6 (3)	Ru(2)-C(6)-O(6)	178.6 (10)	Ru(3)-C(7)-O(7)	176.7 (10)
C(3)-Ru(2)-C(5)	95.0 (4)	Te(1)-Ru(2)-C(6)	160.4 (3)	Ru(3)-C(8)-O(8)	178.6 (9)	Ru(4)-C(9)-O(9)	177.1 (9)
Te(2)-Ru(2)-C(6)	94.9 (3)	Ru(1)-Ru(2)-C(6)	134.4 (3)	Ru(4)-C(10)-O(10)	174.5 (7)		
Ru(4)-Ru(2)-C(6)	106.2 (3)	C(3)-Ru(2)-C(6)	96.8 (4)				

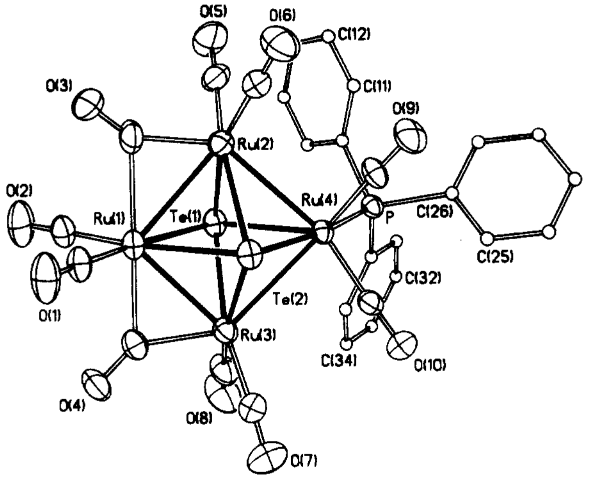
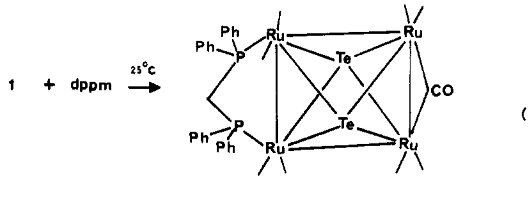


Figure 3. Molecular structure of 3. The carbon atoms of the phenyl rings are drawn as arbitrary radius spheres.

The infrared spectrum of 3 has bands at 2062 (w), 2025 (s), 1997 (w), 1973 (w, sh), 1856 (w), and 1825 (m) cm^{-1}, indicating that 3 contains both terminal and bridging carbonyl groups. Dark brown crystals of 3 were grown from dichloromethane/hexane solutions, and an X-ray analysis was undertaken. An ORTEP diagram of the molecular structure of 3 is shown in Figure 3, and the interatomic bond distances and angles are given in Table VII. The distorted octahedral heavy-atom framework of 3, containing the Ru_4 ring, is similar to that of 1. However, in 3 two adjacent ruthenium–ruthenium bonds are bridged by carbonyl ligands, Ru(1)–Ru(2) = 2.813 (1) Å and Ru(1)–Ru(3) = 2.800 (1) Å, and these bonds are significantly shorter than the unbridged ruthenium–ruthenium bonds, Ru(2)–Ru(4) = 2.962 (1) Å and Ru(3)–Ru(4) = 2.985 (1) Å. The ruthenium–tellurium distances in 3, 2.705–2.800 Å, are similar to the ruthenium–tellurium distances in 1. The metal–tellurium distances to Ru(1), 2.800 (1) and 2.763 (1) Å, are longer than all the others, 2.705–2.751 Å. In the related molecule $Ru_4(\mu_2\text{-}CO)_2(CO)_7(PMe_2Ph)_2(\mu_4\text{-}S)_2$, sulfur also forms longer bonds with the metal atom that is bonded to both bridging carbonyl ligands and is formally eight coordinate than with the other metal atoms that are only seven-coordinate.[8] Each ruthenium atom in 3 contains two terminally coordinated carbonyl ligands. Ru(4), which is not bonded to the bridging carbonyl ligands, also contain a PPh_3 ligand directed out of the Ru_4 plane.

When 1 was stirred with bis(diphenylphosphino)methane (dppm) in dichloromethane solvent for 10 h, a yellow compound (4) was formed (eq 3). The infrared spectrum of 4 in the carbonyl region, 2040 (m), 2009 (s), 1964 (m), and 1790 (w) cm^{-1}, showed that 4 contained terminal and bridging carbonyl ligands. Compound 4 was characterized by X-ray diffraction analysis. An ORTEP drawing of the molecular structure of 4 is shown in Figure 4. The interatomic bond distances and bond angles are given



(3)

4 (32%)

Table VIII. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for **4**

	x	*y*	*z*	U^a		*x*	*y*	*z*	U^a
Te(1)	8579.7 (4)	11597.4 (3)	3170.1 (3)	36.9 (2)	C(41)	5774 (4)	11259 (3)	744 (3)	72 (4)
Te(2)	8815.6 (4)	11628.8 (3)	1234.3 (3)	38.2 (2)	C(42)	5291	10663	629	88 (5)
Ru(1)	8437.9 (4)	12866.1 (3)	1761.6 (3)	31.5 (2)	C(43)	4377	10308	1120	87 (5)
Ru(2)	7171.0 (4)	11393.8 (3)	2425.6 (3)	33.1 (2)	C(44)	3946	10548	1726	75 (5)
Ru(3)	9032.3 (4)	10343.1 (3)	2625.0 (3)	37.0 (2)	C(45)	4429	11144	1841	56 (4)
Ru(4)	10276.5 (4)	11751.4 (3)	2023.2 (3)	40.4 (2)	C(46)	5343	11499	1350	40 (3)
Te(1′)	5216.1 (3)	6047.9 (3)	3926.5 (3)	41.2 (2)	P(1′)	2224 (1)	7746 (1)	4419 (1)	31.2 (7)
Te(2′)	4639.1 (3)	8282.7 (3)	3199.6 (3)	37.8 (2)	P(2′)	2330 (1)	7441 (1)	2933 (1)	32.8 (7)
Ru(1′)	3721.1 (4)	6933.7 (3)	4460.2 (3)	30.4 (2)	O(1′)	2556 (4)	5325 (3)	5429 (3)	67 (3)
Ru(2′)	4026.9 (4)	7047.9 (3)	2863.9 (3)	35.2 (2)	O(2′)	4065 (4)	7016 (4)	5937 (3)	77 (3)
Ru(3′)	6252.7 (5)	7376.2 (4)	2743.7 (4)	47.1 (3)	O(3′)	3763 (5)	5588 (4)	2478 (4)	99 (4)
Ru(4′)	5866.3 (4)	7285.9 (4)	4265.2 (4)	43.3 (3)	O(4′)	4698 (5)	8063 (5)	1132 (3)	111 (4)
P(1)	7650 (1)	13585 (1)	681 (1)	32.7 (7)	O(5′)	7699 (6)	6183 (5)	2247 (5)	127 (5)
P(2)	6045 (1)	12176 (1)	1598 (1)	34.1 (7)	O(6′)	7080 (6)	8802 (5)	1216 (4)	124 (4)
O(1)	7333 (4)	13979 (3)	2537 (3)	67 (3)	O(7′)	8009 (4)	7761 (4)	3335 (4)	78 (3)
O(2)	10291 (4)	13985 (3)	1194 (3)	69 (3)	O(8′)	6889 (5)	6050 (4)	5575 (4)	96 (4)
O(3)	5527 (5)	11138 (4)	3851 (3)	88 (3)	O(9′)	6190 (5)	8670 (5)	4719 (5)	108 (5)
O(4)	6602 (4)	9731 (3)	2501 (4)	81 (3)	C(1′)	2988 (5)	5937 (4)	5058 (4)	42 (3)
O(5)	8679 (4)	8912 (3)	4205 (3)	73 (3)	C(2′)	4047 (6)	7009 (5)	5337 (4)	50 (4)
O(6)	9304 (5)	9087 (4)	1906 (4)	83 (3)	C(3′)	3857 (6)	6138 (5)	2647 (5)	61 (4)
O()	11328 (4)	10058 (3)	2618 (3)	58 (3)	C(4′)	4485 (6)	7663 (6)	1799 (5)	67 (4)
O(8)	11765 (5)	12103 (4)	2852 (4)	96 (4)	C(5′)	7144 (7)	6660 (6)	2423 (5)	75 (5)
O(9)	12005 (5)	12017 (4)	651 (4)	125 (4)	C(6′)	6770 (7)	8282 (6)	1795 (5)	75 (5)
C(1)	7730 (5)	13557 (4)	2253 (4)	45 (3)	C(7′)	7164 (5)	7567 (5)	3396 (5)	55 (4)
C(2)	9646 (5)	13509 (4)	1407 (4)	46 (3)	C(8′)	6496 (6)	6533 (6)	5070 (5)	63 (4)
C(3)	6137 (5)	11259 (5)	3308 (4)	52 (3)	C(9′)	6070 (6)	8137 (6)	4559 (5)	65 (5)
C(4)	6869 (6)	10330 (4)	2485 (5)	60 (4)	C(11′)	3148 (3)	9011 (3)	4612 (3)	50 (4)
C(5)	8815 (5)	9459 (4)	3615 (4)	43 (3)	C(12′)	3175	9801	4612	67 (4)
C(6)	9201 (6)	9563 (4)	2181 (4)	53 (4)	C(13′)	2296	10317	4534	66 (4)
C(7)	10583 (6)	10489 (4)	2484 (4)	46 (3)	C(14′)	1391	10044	4455	66 (4)
C(8)	11194 (6)	11989 (5)	2543 (5)	62 (4)	C(15′)	1365	9255	4455	50 (4)
C(9)	11337 (7)	11940 (5)	1170 (5)	75 (4)	C(16′)	2243	8738	4533	37 (3)
C(11)	7676 (3)	14252 (3)	−957 (3)	52 (3)	C(21′)	1217 (3)	6853 (3)	5915 (3)	58 (4)
C(12)	8569	14473	−1700	58 (4)	C(22′)	367	6539	6505	72 (5)
C(13)	9630	14315	−1787	58 (4)	C(23′)	−615	6622	6321	77 (5)
C(14)	10098	13938	−1132	60 (4)	C(24′)	−746	7019	5546	81 (5)
C(15)	9505	13717	−389	50 (3)	C(25′)	104	7333	4955	60 (4)
C(16)	8444	13875	−301	36 (3)	C(26′)	1086	7250	5140	39 (3)
C(21)	5991 (3)	14742 (3)	739 (3)	55 (4)	C(27′)	1868 (5)	8148 (4)	3436 (4)	37 (3)
C(22)	5606	15513	730	70 (4)	C(31′)	338 (3)	6803 (2)	3291 (3)	53 (4)
C(23)	6283	16140	586	72 (5)	C(32′)	−381	6168	3601	61 (4)
C(24)	7345	15995	452	77 (5)	C(33′)	−70	5341	3991	59 (4)
C(25)	7730	15224	461	59 (4)	C(34′)	960	5149	4070	59 (4)
C(26)	7052	14598	605	37 (3)	C(35′)	1678	5785	3760	42 (3)
C(27)	6648 (5)	12949 (4)	626 (4)	37 (3)	C(36′)	1367	6612	3371	36 (3)
C(31)	5098 (3)	13045 (3)	2501 (3)	48 (3)	C(41′)	2147 (4)	8931 (3)	1618 (3)	55 (4)
C(32)	4341	13566	2703	71 (5)	C(42′)	1946	9402	868	66 (4)
C(33)	3508	13845	2311	72 (5)	C(43′)	1586	9013	466	75 (5)
C(34)	3432	13605	1717	71 (5)	C(44′)	1427	8154	814	87 (5)
C(35)	4189	13084	1515	55 (4)	C(45′)	1628	7683	1563	66 (4)
C(36)	5022	12804	1907	42 (3)	C(46′)	1988	8072	1965	40 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized U_{ij} tensor.

in Table IX. The crystal structure contains two independent but chemically similar molecules. Each molecule consists of the same distorted octahedral Ru_4Te_2 framework as found in **1** and **3**. The shortest edge of the Ru_4 ring, Ru(3)–Ru(4) = 2.807 (1) Å, is bridged by a carbonyl ligand, while the opposite edge, Ru(1)–Ru(2) = 2.904 (1) Å, is bridged by a dppm ligand. The two unbridged sides, Ru(1)–Ru(4) = 2.957 (1) Å and Ru(2)–Ru(3) = 2.919 (1) Å, form the two longest sides of the Ru_4 quadrangle. The ruthenium–tellurium distance is **4**, 2.703–2.780 Å, are similar to the ruthenium–tellurium distances in **1**, 2.691–2.758 Å, and in **3**, 2.705–2.800 Å, but are significantly longer than the ruthenium–tellurium distances involving μ_3-Te ligands in **2**, 2.659–2.702 Å. Each ruthenium atom contains two terminally bonded carbonyl ligands. The chemical environments of the dppm-bridged metal atoms, Ru(2) and Ru(3), differ, as can be seen in the positioning of the carbonyl ligands on these two atoms.

Discussion

When $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$ were refluxed in benzene solvent, transfer of Te ligands and cluster expansion occurred and compound **1** was obtained (eq 1). Compound **1**

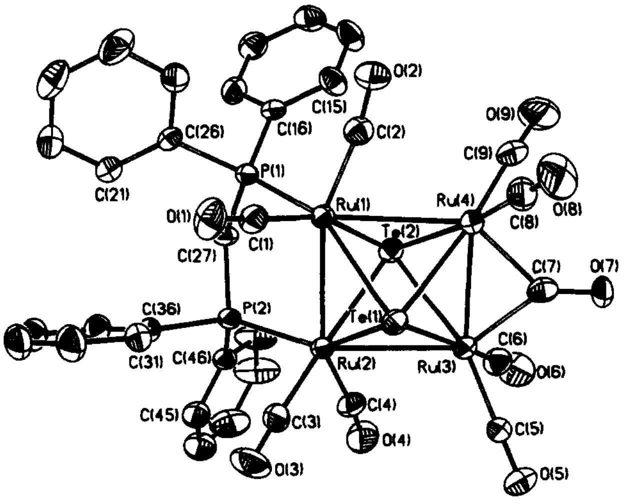


Figure 4. Molecular structure of one of two crystallographically independent molecules of **4**.

Table IX. Selected Bond Distances and Angles for **4**

(a) Bond Distances (Å) for Molecule A

Te(2)–Ru(2)	2.742 (1)	Te(2)–Ru(1)	2.726 (1)	Ru(4)–C(7)	2.052 (7)	Ru(4)–C(8)	1.896 (11)
Te(2)–Ru(4)	2.764 (1)	Te(2)–Ru(3)	2.734 (1)	Ru(4)–C(9)	1.863 (8)	Ru(3)–C(5)	1.876 (6)
Te(1)–Ru(2)	2.703 (1)	Te(1)–Ru(1)	2.725 (1)	Ru(3)–C(6)	1.870 (9)	Ru(3)–C(7)	2.047 (8)
Te(1)–Ru(4)	2.754 (1)	Te(1)–Ru(3)	2.780 (1)	O(1)–C(1)	1.127 (10)	O(2)–C(2)	1.149 (9)
Ru(2)–Ru(1)	2.904 (1)	Ru(2)–Ru(3)	2.918 (1)	O(3)–C(3)	1.136 (9)	O(4)–C(4)	1.133 (11)
Ru(2)–P(2)	2.318 (2)	Ru(2)–C(3)	1.894 (7)	O(5)–C(5)	1.135 (7)	O(6)–C(6)	1.147 (12)
Ru(2)–C(4)	1.908 (9)	Ru(1)–Ru(4)	2.957 (1)	O(7)–C(7)	1.186 (8)	O(8)–C(8)	1.131 (14)
Ru(1)–P(1)	2.328 (2)	Ru(1)–C(1)	1.900 (8)	O(9)–C(9)	1.161 (11)		
Ru(1)–C(2)	1.896 (7)	Ru(4)–Ru(3)	2.807 (1)				

(b) Bond Distances (Å) for Molecule B

Te(1′)–Ru(1′)	2.698 (1)	Te(1′)–Ru(4′)	2.777 (1)	Ru(3′)–C(5′)	1.846 (10)	Ru(4′)–C(7′)	2.075 (7)
Te(1′)–Ru(3′)	2.734 (1)	Te(2′)–Ru(2′)	2.726 (1)	Ru(3′)–C(7′)	2.048 (10)	Ru(4′)–C(9′)	1.869 (12)
Te(2′)–Ru(1′)	2.754 (1)	Te(2′)–Ru(4′)	2.773 (1)	Ru(4′)–C(8′)	1.853 (8)	O(1′)–C(1′)	1.147 (8)
Te(2′)–Ru(3′)	2.755 (1)	Ru(1′)–Ru(4′)	2.889 (1)	O(2′)–C(2′)	1.161 (11)	O(3′)–C(3′)	1.167 (14)
Ru(1′)–Ru(2′)	2.927 (1)	Ru(1′)–C(1′)	1.886 (6)	O(4′)–C(4′)	1.165 (9)	O(5′)–C(5′)	1.171 (14)
Ru(1′)–P(1′)	2.319 (2)	Ru(2′)–Ru(3′)	2.962 (1)	O(6′)–C(6′)	1.134 (10)	O(7′)–C(7′)	1.173 (10)
Ru(1′)–C(2′)	1.879 (9)	Ru(2′)–C(3′)	1.872 (11)	O(8′)–C(8′)	1.167 (11)	O(9′)–C(9′)	1.134 (16)
Ru(2′)–P(2′)	2.324 (2)	Ru(3′)–Ru(4′)	2.799 (1)	Te(1′)–Ru(2′)	2.706 (1)		
Ru(2′)–C(4′)	1.865 (8)	Ru(3′)–C(6′)	1.904 (7)				

(c) Bond Angles (deg) for Molecule A

Ru(2)–Te(2)–Ru(1)	64.2 (1)	Ru(2)–Te(2)–Ru(4)	96.1 (1)	Te(2)–Ru(4)–Te(1)	82.6 (1)	Te(2)–Ru(4)–Ru(1)	56.8 (1)
Ru(1)–Te(2)–Ru(4)	65.2 (1)	Ru(2)–Te(2)–Ru(3)	64.4 (1)	Te(1)–Ru(4)–Ru(1)	56.9 (1)	Te(2)–Ru(4)–Ru(3)	58.8 (1)
Ru(1)–Te(2)–Ru(3)	97.3 (1)	Ru(4)–Te(2)–Ru(3)	61.4 (1)	Te(1)–Ru(4)–Ru(3)	60.0 (1)	Ru(1)–Ru(4)–Ru(3)	90.6 (1)
Ru(2)–Te(1)–Ru(1)	64.7 (1)	Ru(2)–Te(1)–Ru(4)	97.2 (1)	Te(2)–Ru(4)–C(7)	93.7 (2)	Te(1)–Ru(4)–C(7)	92.3 (2)
Ru(1)–Te(1)–Ru(4)	65.3 (1)	Ru(2)–Te(1)–Ru(3)	64.3 (1)	Ru(1)–Ru(4)–C(7)	137.2 (2)	Ru(3)–Ru(4)–C(7)	46.7 (2)
Ru(1)–Te(1)–Ru(3)	96.2 (1)	Ru(4)–Te(1)–Ru(3)	60.9 (1)	Te(2)–Ru(4)–C(8)	171.8 (2)	Te(1)–Ru(4)–C(8)	94.7 (3)
Te(2)–Ru(2)–Te(1)	83.9 (1)	Te(2)–Ru(2)–Ru(1)	57.6 (1)	Ru(1)–Ru(4)–C(8)	115.3 (3)	Ru(3)–Ru(4)–C(8)	126.3 (2)
Te(1)–Ru(2)–Ru(1)	58.0 (1)	Te(2)–Ru(2)–Ru(3)	57.7 (1)	C(7)–Ru(4)–C(8)	94.1 (3)	Te(2)–Ru(4)–C(9)	92.9 (3)
Te(1)–Ru(2)–Ru(3)	59.1 (1)	Ru(1)–Ru(2)–Ru(3)	89.5 (1)	Te(1)–Ru(4)–C(9)	173.7 (3)	Ru(1)–Ru(4)–C(9)	116.9 (2)
Te(2)–Ru(2)–P(2)	93.6 (1)	Te(1)–Ru(2)–P(2)	140.2 (1)	Ru(3)–Ru(4)–C(9)	121.3 (3)	C(7)–Ru(4)–C(9)	92.5 (3)
Ru(1)–Ru(2)–P(2)	87.2 (1)	Ru(3)–Ru(2)–P(2)	147.1 (1)	C(8)–Ru(4)–C(9)	89.2 (4)	Te(2)–Ru(3)–Te(1)	82.6 (1)
Te(2)–Ru(2)–C(3)	173.5 (3)	Te(1)–Ru(2)–C(3)	89.6 (3)	Te(2)–Ru(3)–Ru(2)	57.9 (1)	Te(1)–Ru(3)–Ru(2)	56.6 (1)
Ru(1)–Ru(2)–C(3)	118.1 (3)	Ru(3)–Ru(2)–C(3)	119.2 (2)	Te(2)–Ru(3)–Ru(4)	59.8 (1)	Te(1)–Ru(3)–Ru(4)	59.1 (1)
P(2)–Ru(2)–C(3)	90.9 (2)	Te(2)–Ru(2)–C(4)	93.3 (2)	Ru(2)–Ru(3)–Ru(4)	91.3 (1)	Te(2)–Ru(3)–C(5)	165.4 (2)
Te(1)–Ru(2)–C(4)	122.9 (3)	Ru(1)–Ru(2)–C(4)	150.9 (2)	Te(1)–Ru(3)–C(5)	95.2 (3)	Ru(2)–Ru(3)–C(5)	108.9 (2)
Ru(3)–Ru(2)–C(4)	71.5 (2)	P(2)–Ru(2)–C(4)	96.9 (3)	Ru(4)–Ru(3)–C(5)	130.9 (3)	Te(2)–Ru(3)–C(6)	91.8 (2)
C(3)–Ru(2)–C(4)	90.7 (4)	Te(2)–Ru(1)–Te(1)	83.8 (1)	Te(1)–Ru(3)–C(6)	172.5 (2)	Ru(2)–Ru(3)–C(6)	116.2 (3)
Te(2)–Ru(1)–Ru(2)	58.2 (1)	Te(1)–Ru(1)–Ru(2)	57.3 (1)	Ru(4)–Ru(3)–C(6)	122.1 (2)	C(5)–Ru(3)–C(6)	89.0 (3)
Te(2)–Ru(1)–Ru(4)	58.0 (1)	Te(1)–Ru(1)–Ru(4)	57.8 (1)	Te(2)–Ru(3)–C(7)	94.7 (2)	Te(1)–Ru(3)–C(7)	91.6 (2)
Ru(2)–Ru(1)–Ru(4)	88.6 (1)	Te(2)–Ru(1)–P(1)	85.8 (1)	Ru(2)–Ru(3)–C(7)	138.0 (2)	Ru(4)–Ru(3)–C(7)	46.9 (2)
Te(1)–Ru(1)–P(1)	153.3 (1)	Ru(2)–Ru(1)–P(1)	96.5 (1)	C(5)–Ru(3)–C(7)	99.8 (3)	C(6)–Ru(3)–C(7)	93.8 (3)
Ru(4)–Ru(1)–P(1)	133.3 (1)	Te(2)–Ru(1)–C(1)	160.5 (2)	Ru(1)–C(1)–O(1)	178.2 (7)	Ru(1)–C(2)–O(2)	170.9 (6)
Te(1)–Ru(1)–C(1)	91.1 (2)	Ru(2)–Ru(1)–C(1)	103.4 (2)	Ru(2)–C(3)–O(3)	176.7 (7)	Ru(2)–C(4)–O(4)	173.5 (7)
Ru(4)–Ru(1)–C(1)	133.3 (2)	P(1)–Ru(1)–C(1)	90.5 (2)	Ru(3)–C(5)–O(5)	178.3 (8)	Ru(3)–C(6)–O(6)	179.7 (6)
Te(2)–Ru(1)–C(2)	107.3 (3)	Te(1)–Ru(1)–C(2)	108.6 (2)	Ru(4)–C(7)–Ru(3)	86.4 (3)	Ru(4)–C(7)–O(7)	135.7 (6)
Ru(2)–Ru(1)–C(2)	158.6 (2)	Ru(4)–Ru(1)–C(2)	70.0 (2)	Ru(3)–C(7)–O(7)	137.8 (6)	Ru(4)–C(8)–O(8)	177.1 (8)
P(1)–Ru(1)–C(2)	97.9 (2)	C(1)–Ru(1)–C(2)	92.2 (3)	Ru(4)–C(9)–O(9)	176.7 (8)		

(d) Bond Angles (deg) for Molecule B

Ru(1′)–Te(1′)–Ru(2′)	65.5 (1)	Ru(1′)–Te(1′)–Ru(3′)	97.2 (1)	Te(1′)–Ru(3′)–Te(2′)	83.1 (1)	Te(1′)–Ru(3′)–Ru(2′)	56.6 (1)
Ru(2′)–Te(1′)–Ru(3′)	66.0 (1)	Ru(1′)–Te(1′)–Ru(4′)	63.7 (1)	Te(2′)–Ru(3′)–Ru(2′)	56.8 (1)	Te(1′)–Ru(3′)–Ru(4′)	60.2 (1)
Ru(2′)–Te(1′)–Ru(4′)	97.1 (1)	Ru(3′)–Te(1′)–Ru(4′)	61.0 (1)	Te(2′)–Ru(3′)–Ru(4′)	59.9 (1)	Ru(2′)–Ru(3′)–Ru(4′)	91.0 (1)
Ru(1′)–Te(2′)–Ru(2′)	64.6 (1)	Ru(1′)–Te(2′)–Ru(3′)	95.4 (1)	Te(1′)–Ru(3′)–C(5′)	90.6 (2)	Te(2′)–Ru(3′)–C(5′)	169.3 (3)
Ru(2′)–Te(2′)–Ru(3′)	65.4 (1)	Ru(1′)–Te(2′)–Ru(4′)	63.0 (1)	Ru(2′)–Ru(3′)–C(5′)	112.5 (3)	Ru(4′)–Ru(3′)–C(5′)	123.9 (3)
Ru(2′)–Te(2′)–Ru(4′)	96.7 (1)	Ru(3′)–Te(2′)–Ru(4′)	60.8 (1)	Te(1′)–Ru(3′)–C(6′)	167.7 (3)	Te(2′)–Ru(3′)–C(6′)	95.0 (3)
Te(1′)–Ru(1′)–Te(2′)	83.8 (1)	Te(1′)–Ru(1′)–Ru(2′)	57.3 (1)	Ru(2′)–Ru(3′)–C(6′)	112.4 (3)	Ru(4′)–Ru(3′)–C(6′)	129.0 (4)
Te(2′)–Ru(1′)–Ru(2′)	57.3 (1)	Te(1′)–Ru(1′)–Ru(4′)	59.5 (1)	C(5′)–Ru(3′)–C(6′)	89.3 (4)	Te(1′)–Ru(3′)–C(7′)	96.5 (2)
Te(2′)–Ru(1′)–Ru(4′)	58.8 (1)	Ru(2′)–Ru(1′)–Ru(4′)	89.9 (1)	Te(2′)–Ru(3′)–C(7′)	92.1 (2)	Ru(2′)–Ru(3′)–C(7′)	138.4 (2)
Te(1′)–Ru(1′)–P(1′)	154.6 (1)	Te(2′)–Ru(1′)–P(1′)	87.2 (1)	Ru(4′)–Ru(3′)–C(7′)	47.6 (2)	C(5′)–Ru(3′)–C(7′)	97.2 (4)
Ru(2′)–Ru(1′)–P(1′)	98.0 (1)	Ru(4′)–Ru(1′)–P(1′)	133.1 (1)	C(6′)–Ru(3′)–C(7′)	95.7 (4)	Te(1′)–Ru(4′)–Te(2′)	82.0 (1)
Te(1′)–Ru(1′)–C(1′)	88.8 (2)	Te(2′)–Ru(1′)–C(1′)	161.1 (3)	Te(1′)–Ru(4′)–Ru(1′)	56.8 (1)	Te(2′)–Ru(4′)–Ru(1′)	58.2 (1)
Ru(2′)–Ru(1′)–C(1′)	104.3 (3)	Ru(4′)–Ru(1′)–C(1′)	130.6 (2)	Te(1′)–Ru(4′)–Ru(3′)	58.7 (1)	Te(2′)–Ru(4′)–Ru(3′)	59.3 (1)
P(1′)–Ru(1′)–C(1′)	92.2 (2)	Te(1′)–Ru(1′)–C(2′)	109.3 (2)	Ru(1′)–Ru(4′)–Ru(3′)	91.5 (1)	Te(1′)–Ru(4′)–C(7′)	94.6 (3)
Te(2′)–Ru(1′)–C(2′)	105.4 (2)	Ru(2′)–Ru(1′)–C(2′)	156.9 (2)	Te(2′)–Ru(4′)–C(7′)	91.0 (2)	Ru(1′)–Ru(4′)–C(7′)	138.3 (3)
Ru(4′)–Ru(1′)–C(2′)	67.2 (2)	P(1′)–Ru(1′)–C(2′)	96.0 (2)	Ru(3′)–Ru(4′)–C(7′)	46.8 (3)	Te(1′)–Ru(4′)–C(8′)	93.7 (4)
C(1′)–Ru(1′)–C(2′)	93.4 (3)	Te(1′)–Ru(2′)–Te(2′)	84.2 (1)	Te(2′)–Ru(4′)–C(8′)	170.9 (2)	Ru(1′)–Ru(4′)–C(8′)	112.8 (3)
Te(1′)–Ru(2′)–Ru(1′)	57.1 (1)	Te(2′)–Ru(2′)–Ru(1′)	58.2 (1)	Ru(3′)–Ru(4′)–C(8′)	125.0 (3)	C(7′)–Ru(4′)–C(8′)	97.3 (3)
Te(1′)–Ru(2′)–Ru(3′)	57.5 (1)	Te(2′)–Ru(2′)–Ru(3′)	57.8 (1)	Te(1′)–Ru(4′)–C(9′)	170.6 (2)	Te(2′)–Ru(4′)–C(9′)	93.8 (3)
Ru(1′)–Ru(2′)–Ru(3′)	87.6 (1)	Te(1′)–Ru(2′)–P(2′)	133.9 (1)	Ru(1′)–Ru(4′)–C(9′)	113.8 (2)	Ru(3′)–Ru(4′)–C(9′)	126.0 (3)
Te(2′)–Ru(2′)–P(2′)	95.4 (1)	Ru(1′)–Ru(2′)–P(2′)	83.7 (1)	C(7′)–Ru(4′)–C(9′)	93.9 (4)	C(8′)–Ru(4′)–C(9′)	89.3 (4)
Ru(3′)–Ru(2′)–P(2′)	152.0 (1)	Te(1′)–Ru(2′)–C(3′)	89.4 (2)	Ru(1′)–C(1′)–O(1′)	178.8 (7)	Ru(1′)–C(2′)–O(2′)	167.7 (6)
Te(2′)–Ru(2′)–C(3′)	171.9 (2)	Ru(1′)–Ru(2′)–C(3′)	121.8 (2)	Ru(2′)–C(3′)–O(3′)	176.6 (7)	Ru(2′)–C(4′)–O(4′)	176.5 (8)
Ru(3′)–Ru(2′)–C(3′)	114.5 (2)	P(2′)–Ru(2′)–C(3′)	92.6 (2)	Ru(3′)–C(5′)–O(5′)	177.5 (7)	Ru(3′)–C(6′)–O(6′)	177.4 (1)
Te(1′)–Ru(2′)–C(4′)	128.4 (3)	Te(2′)–Ru(2′)–C(4′)	91.4 (4)	Ru(3′)–C(7′)–Ru(4′)	85.5 (3)	Ru(3′)–C(7′)–O(7′)	139.3 (7)
Ru(1′)–Ru(2′)–C(4′)	149.4 (4)	Ru(3′)–Ru(2′)–C(4′)	76.9 (3)	Ru(4′)–C(7′)–O(7′)	135.2 (8)	Ru(4′)–C(8′)–O(8′)	179.0 (10)
P(2′)–Ru(2′)–C(4′)	97.7 (3)	C(3′)–Ru(2′)–C(4′)	88.7 (4)	Ru(4′)–C(9′)–O(9′)	177.9 (7)		

Inorg. Chem. **1990**, *29*, 4665–4671

underwent room-temperature substitution reactions with PPh_3 to form compounds **2** and **3** (eq 2) and with dppm to form compound **4** (eq 3).

Compounds **1**, **3**, and **4** contain only 62 valence electrons each, and thus are formally electron deficient by 2 electrons, according to the 18-electron rule. They do however obey the PSEP theory,[10] according to which the core of each cluster (including the Te ligands) is an octahedron, requiring the presence of 14 cluster valence electrons. Compounds **1**, **3**, and **4**, have 7 SEPs required for the octahedral geometry. Compound **2** contains 50 electrons and to be electron precise, on the basis of the 18-electron rule, should contain only two metal–metal bonds, as observed. The PSEP theory also seems to apply well in the case of **2**. According to this theory the cluster core of **2**, including the Te ligands, has the form of a nido octahedron, requiring the presence of 7 SEPs, which this cluster has.

The known isoelectronic clusters $Fe_4(CO)_{10}(\mu\text{-}CO)(\mu\text{-}PPh)_2$[11] and $Ru_4(CO)_{11}(\mu\text{-}CO)(\mu\text{-}PPh)_2$[12] contain square arrangements of the four metal atoms with quadruply bridging phosphinidene ligands on opposite sides of the cluster and have the bridging carbonyl ligand associated with the shortest metal–metal bond. It has been proposed that this shortening could be due to the influence of the bridging ligand. The unsaturation of the iron bis(phosphinidene) cluster was demonstrated by the ease with which it adds a two-electron ligand, L (L = CO, $P(OMe)_3$, *t*-BuNC), to form the saturated clusters $Fe_4(CO)_{11}L(\mu\text{-}PPh)_2$. The latter, however, are not significantly more stable because they quantitatively loss one CO under vacuum to give the substituted derivatives, $Fe_4(CO)_{10}L(\mu\text{-}PPh)_2$.[13] When **1** was treated with phosphines, we did not observe any addition products.

Although it is not possible at present to predict the mechanism of formation of **1** from $Fe_3(CO)_9(\mu_3\text{-}Te)_2$ and $Ru_3(CO)_{12}$, a mixed-metal intermediate containing both iron and ruthenium atoms bridged by tellurium ligands may be involved. The involvement of such mixed-metal intermediates in the overall atom-transfer reactions has been observed in the formation of $Os_3(CO)_9(\mu_3\text{-}Te)_2$ from the reaction of $Fe_2(CO)_6(\mu_2\text{-}Te_2)$ and $Os_3(CO)_{11}(NCMe)$, which proceeds via an initial formation of $Fe_2Os_3(CO)_{17}(\mu_4\text{-}Te)(\mu_3\text{-}Te)$.[5] Attempts are presently being made to identify any such intermediates in the formation of compound **1**.

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Supplementary Material Available: Tables of complete crystal, data collection, and refinement parameters, bond distances and angles, anisotropic thermal parameters, and hydrogen coordinates and thermal parameters for **1–4** (21 pages); tables of observed and calculated structure factors for **1–4** (121 pages). Ordering information is given on any current masthead page.

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Comparison of the $[M^{IV}(RR'dtc)_3]^+/M^{III}(RR'dtc)_3$ and $[M^{IV}(Et_2dsc)_3]^+/M^{III}(Et_2dsc)_3$ (M = Co, Rh, Ir; dtc = Dithiocarbamate; dsc = Diselenocarbamate) Redox Couples and the Reactivity of the Oxidation State IV Complexes in Solution and in the Gas Phase As Studied by Electrochemical and Mass Spectrometric Techniques

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A range of $Ir^{III}(RR'dtc)_3$ complexes (RR'dtc = dithiocarbamate) and $Ir^{III}(Et_2dsc)_3$ (dsc = diselenocarbamate) have been synthesized. The $[Ir^{IV}(RR'dtc)_3]^+$ and $[Ir^{IV}(Et_2dsc)_3]^+$ oxidized species have been prepared and studied in solution by electrochemical techniques and in the gas phase by mass spectrometry. Voltammetric studies at platinum disk electrodes in dichloromethane, acetone, and acetonitrile enable the standard redox potentials ($E°$) for the $[Ir(RR'dtc)_3]^+/Ir(RR'dtc)_3$ couple (and the selenium analogue) to be calculated from the chemically reversible one-electron-oxidation process $Ir(RR'dtc)_3 \rightleftharpoons [Ir(RR'dtc)_3]^+ + e^-$. Comparison with data for the corresponding cobalt and rhodium complexes shows the $E°$ values to have the unexpected order Rh > Co > Ir with the rhodium couple being the most positive. Bulk electrolysis at platinum-gauze electrodes enables the Ir(IV) complexes to be characterized in dichloromethane solution. $[Ir(RR'dtc)_3]^+$ is stable on the synthetic time scale whereas $[Ir(Et_2dsc)_3]^+$ slowly dimerizes during the course of bulk electrolysis experiments and subsequently undergoes an internal redox reaction to give $[Ir_2(Et_2dsc)_5]^+$ and oxidized ligand, as previously observed for cobalt and rhodium dithiocarbamate and diselenocarbamate complexes. The order of the rates of these redox-based decomposition reactions is Rh ≫ Co ≫ Ir, which leads to the unusual result that Rh(IV) is considerably more reactive than Co(IV), with the high stability of Ir(IV) being as expected. That is, in this case, the thermodynamic and kinetic stabilities are parallel. The strong oxidizing power of the $[Ir(RR'dtc)_3]^+$ cations is illustrated by their oxidation of free dithiocarbamate ion to give thiuram disulfide and by the oxidation of elemental mercury to give mixed-metal complexes $Hg + 2[Ir(RR'dtc)_3]^+ \rightarrow [HgIr_2(RR'dtc)_6]^{2+}$. The mixed mercury/iridium complexes are also generated electrochemically at mercury electrodes by the reversible process $Hg + 2Ir(RR'dtc)_3 \rightleftharpoons [HgIr_2(RR'dtc)_6]^{2+} + 2e^-$. Generation of $[M(RR'dtc)_3]^+$ (M = Co, Rh, Ir) in the gas phase by positive ion mass spectrometry reveals the expected order of reactivity Ir < Rh < Co. The differences between the solution and gas-phase reactivities of the oxidation state IV complexes are explained by the presence of dimerization reactions in solution, which cannot occur under the conditions of mass spectrometry.

Introduction

Little is known about the quantitative aspects of the higher oxidation state solution chemistry of the group 9 metals (Co, Rh, Ir). Thus, in a very recent paper, Sykes et al.[3] noted the paucity of information about the solution chemistry of iridium in its higher oxidation states, despite the fact that numerous studies on the oxidation of Ir(III) complexes have been reported. Typically, the products of oxidation of Ir(III) complexes have not been well

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