(Tellurolato)chromium Complexes. Syntheses and Crystal Structures of $CpCr(CO)_3(TePh)$, $[CpCr(CO)_2(TePh)]_2$, and $[CpCr(TePh)]_2Te$

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The predominant product isolated from the reaction of $[CpCr(CO)_3]_2$ (**1**; Cp = η^5-C_5H_5) with 1 molar equiv of Ph_2Te_2 varies with reaction conditions as follows: $CpCr(CO)_3(TePh)$ (**2**; 67% yield, from an instantaneous reaction at ambient temperature), $[CpCr(CO)_2(TePh)]_2$ (**3**; 80% yield, after 4.5 h at 60 °C), and $[CpCr(TePh)]_2Te$ (**4**; 70% yield, after 4 h at 80 °C). Thermolysis studies showed an interconversion between **2** and **3**, accompanied by slow total decarbonylation to **4**. An NMR-tube reaction of $[CpCr(CO)_2]_2$ with Ph_2Te_2 at 70 °C for 2 h resulted in the formation of **2** (58%), **3** (4%), and **4** (34%). The complexes, **2**–**4** have been elementally, spectrally, and structurally characterized. Crystal data: **2**, monoclinic, space group $P2_1/c$, a = 10.8250(8) Å, b = 8.6891(6) Å, c = 15.5263(7) Å, β = 98.880(5)°, V = 1442.9(2) Å^3, Z = 4; **3**, triclinic, space group $P\bar{1}$, a = 10.0493(8) Å, b = 11.0612(6) Å, c = 13.263(1) Å, α = 102.021(6)°, β = 93.791(7)°, γ = 105.652(5)°, V = 1376.7(2) Å^3, Z = 2; **4**, monoclinic, space group $P2_1/n$, a = 10.1595(7) Å, b = 21.505(1) Å, c = 10.615(1) Å, β = 95.607(8)°, V = 2308.1(5) Å^3, Z = 4.

Introduction

Although the occurrence of thiolate ligands in transition-metal complexes is frequently reported, complexes containing selenolato and tellurolato ligands are relatively scarce. A few examples are known of tellurolato complexes, and these have been derived from the interaction of Ph_2Te_2 with $[(\eta^5\text{-}RC_5H_4)Mo(CO)_3]_2$ (R = H,[1] R = Me[2]), $[CpFe(CO)_2]_2$,[3] and more recently with $[PtX(CH_3)_3]_4$ (X = Br, I).[4] As part of our continuing investigation of the interaction of $[CpCr(CO)_3]_2$ (**1**) with diphenyl dichalcogenides,[5,6] we have extended this study to diphenyl ditelluride and herein report the results.

Results and Discussion

Synthetic Studies. A deep green suspension of $[CpCr(CO)_3]_2$ (**1**) in toluene reacted instantaneously with 1 molar equiv of Ph_2Te_2 at ambient temperature to give a brownish green homogeneous solution, from which were isolated green crystals of $CpCr(CO)_3(TePh)$ (**2**) in *ca.* 67% yield and trace amounts of $[CpCr(CO)_2(TePh)]_2$ (**3**). An identical reaction after 4.5 h at 60 °C gave the compounds **2** and **3** in *ca.* 10 and 80% yields, respectively. Another similar reaction after 4 h at 80 °C led to the isolation of **3** and $[CpCr(TePh)]_2Te$ (**4**) in ca. 30 and 70% yields, respectively.

An NMR spectral study showed that the compounds **2**–**4** were also formed from the reaction of the Cr≡Cr triply bonded dimer $[CpCr(CO)_2]_2$, with 1 molar equiv of Ph_2Te_2. Thus, a 20 mM solution of $[CpCr(CO)_2]_2$ in C_6D_6 was found to have undergone a 96% conversion to **2**–**4** in 58, 4, and 34% yields, respectively, after *ca.* 2 h at 70 °C.

Product Characterization. The compounds **2**–**4** have been fully characterized via elemental analyses, spectral data, and single-crystal X-ray diffraction analyses. While the mononuclear complex **2** shows a singlet Cp resonance in both its ^1H and ^{13}C NMR spectra, as expected, it was found that the dinuclear complex **3** also exhibits only a singlet Cp resonance. In both complexes, the proton chemical shift of the Cp resonance is slightly temperature dependent over the range 30–75 °C. In their IR spectra, the pattern and relative intensities of CO stretching frequencies of **2** correlate very well with those of its Se analogue (2000 vs, 1940 vs, and 1920 vs cm^{-1}), while those of **3** resemble closely those of its S analogue (1945 vs, 1920 vs, 1870 vs, and 1850 s cm^{-1}),[5] suggesting similar molecular geometries and symmetries of the analogues, as was also shown by their crystal structures described below. The FAB$^+$ mass spectrum of **3** (Figure 1A) gives the molecular ion and shows the stepwise simultaneous loss of 2 CO's, followed by loss of a Ph ring to give $Cp_2Cr_2Te_2Ph$. The exact match of the observed and calculated isotopic distribution pattern is illustrated in Figure 1B. The FAB$^+$ spectrum of **2** shows its molecular ion and the loss of 3 CO's in a single step to give CpCr(TePh) as the most intense fragment. In their EI mass spectra, the molecular ion of **3** is extremely weak and that of **2** is not observed at all. Instead, the highest prominent peak in both (m/z 410) possesses the isotopic distribution pattern of $(C_6H_5)_2Te$ (Figure 1C), followed by m/z 282 ($(C_6H_5)_2Te$) and 207 ($(C_6H_5)Te$).

The non-carbonyl compound **4**, $[CpCr(TePh)]_2$, has been isolated as green crystals, unlike the purple crystals of its S[5] and Se[6b] analogues. As distinct from the single broad Cp resonances of the S and Se analogues at δ 13.24 ($\nu_{1/2}$ = 78 Hz) and δ 15.91 ($\nu_{1/2}$ = 66 Hz), respectively, the ^1H NMR spectrum of **4** over the temperature range from −90 to +80 °C shows two broad Cp resonances. Both peaks maintain approximately equal relative intensity through-

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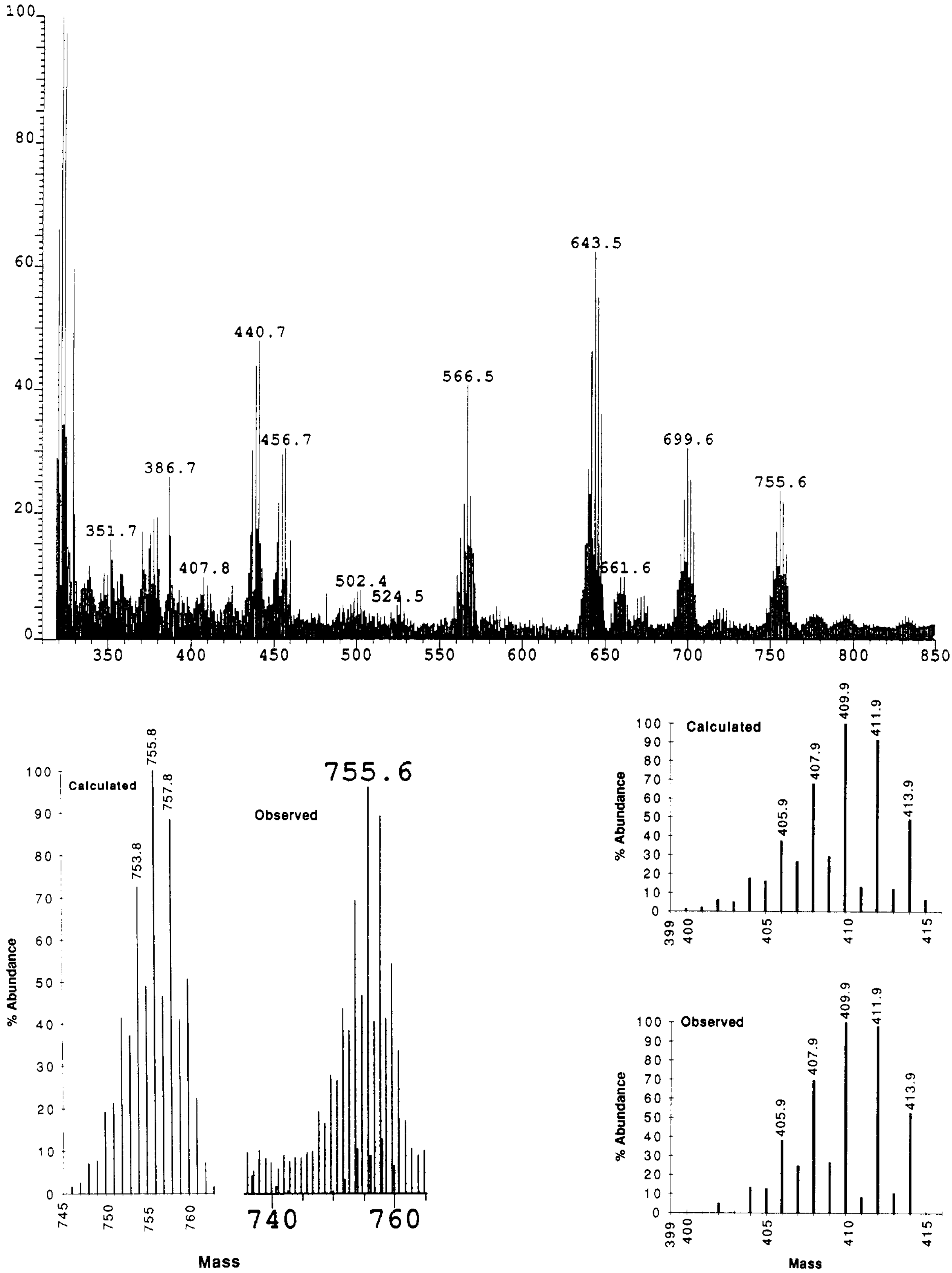
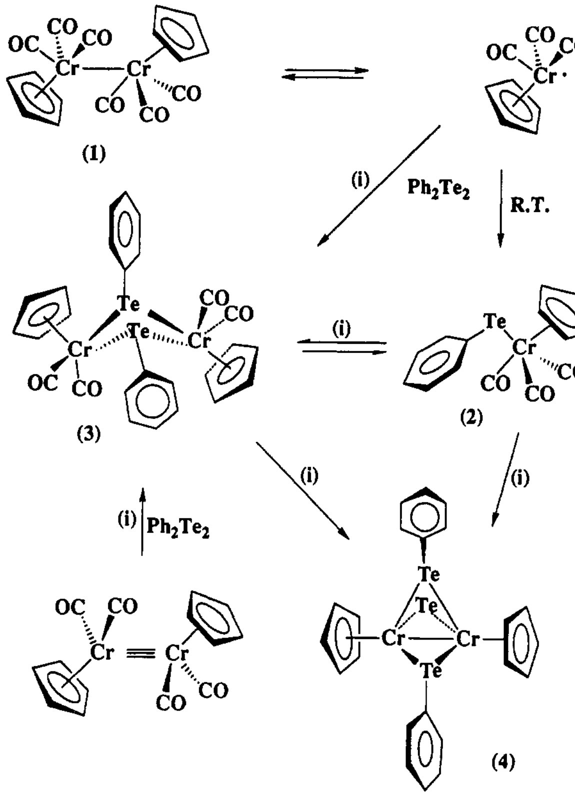


Figure 1. (A, top) FAB+ mass spectrum of 3. (B, bottom left) Observed and calculated isotopic distribution patterns of 3. (C, bottom right) Observed and calculated isotopic distribution patterns of $(C_6H_5)_2Te$.

out the temperature range studied and undergo downfield shifts of similar magnitudes with a rise in temperature. These observations support the existence of two distinct species in solution. Whether crystalline samples of 4 exist in one isomeric form or as a mixture of two remains uncertain, though the observation of two Cp resonances in a solution sample prepared and scanned at −90 °C would seem to suggest the presence of a mixture. It is evident that it is not possible to assign the particular Cp proton resonance pertaining to the structurally determined isomer described below. The broad character and the large temperature dependence of the chemical shifts of the proton Cp resonances suggest paramagnetism. Unfortunately, the presence of isomers would make any attempts at investigation futile. In this context, however, one may note that the similar complex $[CpCr(SCMe_3)]_2S$[25] and its

Scheme 1 [a]



[a] Legend: (i) 60–80 °C.

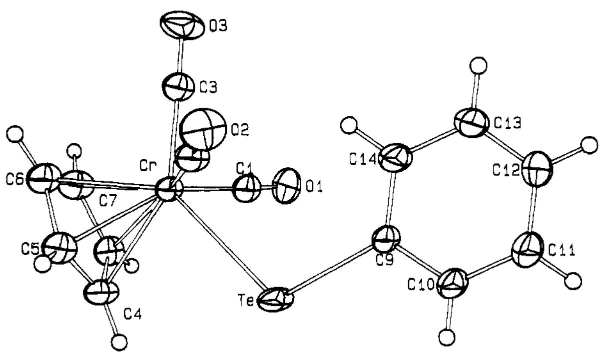


Figure 2. Molecular structure of $CpCr(CO)_3(TePh)$ (2).

derivatives[26] have been found to be antiferromagnetic. The ^{13}C Cp resonances of the two isomers are observed as an unresolved broad singlet, much broader than those of the S and Se compounds at δ 100.44 and 99.22, respectively. Both the EI and FAB$^+$ mass spectra of 4 do not give the molecular ion or show any meaningful fragmentation pattern.

Thermolytic Degradations: An NMR Study. $CpCr(CO)_3(TePh)$ (2). At *ca.* 60 °C in the NMR probe, a 10 mM solution of **2** in C_6D_6 showed a slow conversion to the dinuclear species $[CpCr(CO)_2(TePh)]_2$ (**3**), reaching 17% after 6 h, accompanied by minute traces of the complex **4**. Formation of **4** reached 8% after 17 h and 90% after 37 h.

In a second experiment, a solution of **2** after 40 min at 80 °C showed in its proton NMR spectrum a 10% conversion to **3**, the relative quantity of which slowly decreased to zero within 2.5 h, accompanied by *ca.* 20% conversion of the starting complex **2** to thermolyzed products. After 9 h there was 80% conversion to the compound **4**, in addition to small amounts of other Cp-containing species.

$[CpCr(CO)_2(TePh)]_2$ (3). At *ca.* 78 °C in the NMR probe, a 2 mM solution of **3** in C_6D_6 underwent conversion to mixtures of **3** and **2** as follows: 1:1 molar equiv (1 min), 4:1 molar equiv (3 min), and 7:3 molar equiv (28 min). After 1.5 h, 50% decomposition to **4** had occurred, leaving behind a 2:3 molar equiv mixture of **3** and **2**. Complete conversion to **4** took *ca.* 15 h. A more concentrated 30 mM solution undergoes a higher conversion to **2** (20 min, 23%; 40 min, 50%; 60 min, 63%), before thermolysis to **4**.

Reaction Pathways. The nature of the products obtained under various conditions of synthesis and the results of thermolytic studies are consistent with reaction pathways illustrated in Scheme 1. Consistent with our earlier proposals for reactions of compound **1** with S_8,[7] Se_8,[8] Ph_2S_2,[5] Ph_2Se_2,[6] P_4,[9] and As_4,[10] the facile nature of the reaction of **1** with Ph_2Te_2 must arise from the appreciable concentration of the extremely reactive 17e radical species $CpCr(CO)_3^{\bullet}$ in solution[11–15] and the susceptibility of the Te–Te bond in Ph_2Te_2 to radical cleavage, as was observed for Ph_2S_2[5] and Ph_2Se_2.[6] In the absence of such a radical mechanism, the reactions of Ph_2Te_2 with transition-metal complexes had generally necessitated more forcing conditions.[1–3] The isolation of compound **2** as the principal product under mild reaction conditions and of **3** and **4**, respectively, as the major products under progressively more rigorous conditions suggests that the mononuclear complex **2** is the primary product, as was the case in the analogous reaction with Ph_2Se_2.[6] Indeed, thermolysis studies at 60 °C via NMR spectral observations showed a 17% conversion of **2** after 6 h to the dimeric tellurido-bridged complex **3**, before degradation to the non-carbonyl-containing complex **4** was observed to set in. The partial loss of CO to form the intermediate $[CpCr(CO)(TePh)]_2$ was not observed, though the S and Se analogues were readily isolated in moderate yields after 3 h at 50–60 °C. Total degradation of **3** to **4** took more than 37 h at 60 °C. At 80 °C, the formation of **3** as an intermediate was not obvious, indicating similar rates for its formation and decomposition. The sequence of products described above is also reminiscent of that obtained from the analogous reaction of $[CpMo(CO)_3]_2$ under various reaction conditions, i.e. $CpMo(CO)_3(TePh)$ from infrared irradiation at 25 °C after 3 h, $[CpMo(CO)_2(TePh)]_2$ from refluxing benzene after 14 h, and the completely decarbonylated compound $[CpMo(TePh)_2]_x$ from refluxing xylene after 5 h.[1] Likewise, UV irradiation of Ph_2Te_2 in the presence of $[(MeCp)Mo(CO)_3]_2$ had yielded the doubly μ-TePh bridged complex $[CpMo(CO)_2(TePh)]_2$, which underwent decarbonylation by mild thermolysis in vacuo to give $[CpMo(CO)(TePh)]_2$ in good yield.[2] Similarly, the reaction of Ph_2Te_2 with $[CpFe(CO)_2]_2$ for 3 h in refluxing benzene gave initially the mononuclear complex CpFe-

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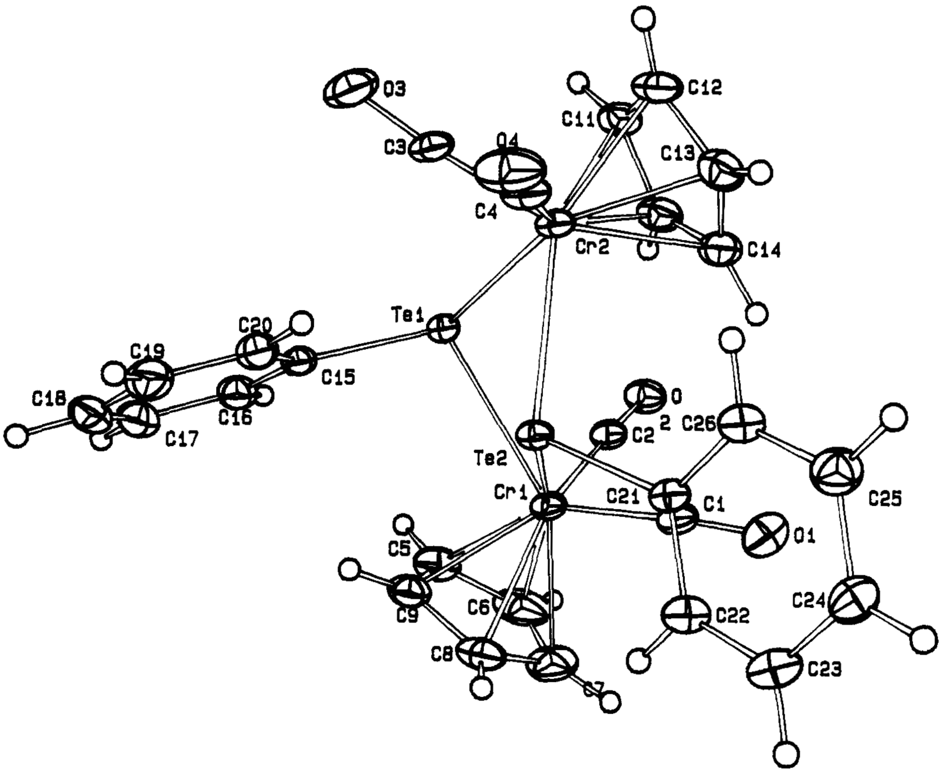

Figure 3. Molecular structure of $[CpCr(CO)_2(TePh)]_2$ (**3**) without the $^1/_2$ C_6H_6 molecule of solvation.

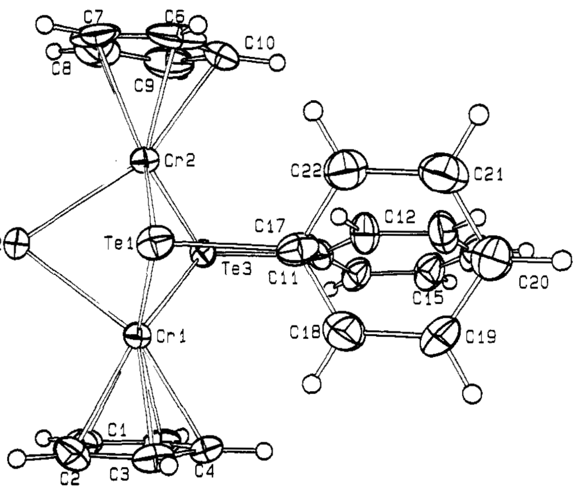

Figure 4. Molecular structure of $[CpCr(TePh)]_2Te$ (**4**).

$(CO)_2(TePh)$, which converted to the dinuclear complex $[CpFe(CO)(TePh)]_2$ under IR irradiation.[3] As observed previously for $[CpMo(CO)_3(EPh)]$[1] and $CpFe(CO)_2$-$(TePh)$,[3] the ease of dimerization of $CpCr(CO)_3(EPh)$ with loss of CO follows the order E = S > Se > Te.

A rather unexpected observation, not seen in the analogous S[5] and Se[6] systems, was the reverse formation of **2** from the dinuclear complex **3** at 78 °C. An approximately 1:1 molar equiv mixture was formed within minutes, after which the relative proportion of **2** decreased as decomposition progressed, reaching 50% after 1.5 h. This reverse process is probably the main reason for the insignificant presence of **3** in the thermolysis of **2** at 80 °C, as noted above.

In view of these reverse processes between **2** and **3**, it is difficult to ascertain which of them is the precursor complex to the non-carbonyl compound **4** (Scheme 1).

Structures. The Ortep plots of the molecular structures of **2–4** are illustrated in Figure 2–4, respectively. Their positional parameters are given in Table 1. Selected bonding parameters are presented in Tables 2–4.

The structure of **2** shows a strong resemblance to its Se analogue,[6] both possessing a four-legged piano-stool geometry around Cr, which achieves an 18-electron configuration. A comparison of some selected bonding parameters are given in Table 5. The Cr–Te distance (2.7634 Å) is shorter than the sum of the single-bond radii of Cr (1.48 Å)[16] and Te (1.36 or 1.41 Å, which is half the Te–Te bonded distance in Ph_2Te_2[17]). The difference (0.175 Å) in the Cr–Te and Cr–Se distances is less than the difference (0.20 Å) between the covalent radii of the chalcogens.

The complex **3** is isostructural with its sulfur analogue,[5] and the bonding parameters of their M_2E_2 cores are listed in Table 6, together with those of $[CpMo(TePh)]_2$.[18] As in the S analogue, the Cr_2Te_2 fragment is nonplanar, with dihedral angles of 123.18(2)° between the Cr1–Te1–Cr2 and Cr1–Te2–Cr2 planes. The Cr1···Cr2 separation of 4.112(1) Å is much longer than that found in the S analogue (3.808 Å),[5] both consistent with the nonexistence of any M–M bond.

The crystal and molecular structure of $[CpCr(TePh)]_2Te$ (**4**) is different from those of its S and Se analogues in its crystal class (monoclinic versus triclinic) and the absence of incorporated solvent molecules.[5,6b] The geometries about the Cr centers are quite similar in all three analogues. However, in the Te complex, the size of the PhE–Cr–EPh angle exceeds those of the other two PhE–Cr–E angles by about 20°, an observation not found in the S and Se analogues. The origin for this difference lies in the much closer disposition of the two phenyl rings (C20–C14 = 5.13 Å) in **4** than in its S and Se analogues (9.67 and 9.82 Å, respectively).

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Table 1. Positional and Equivalent Displacement Parameters for Compounds 2–4

atom	x	y	z	B (Å²)[a]	atom	x	y	z	B (Å²)[a]
				(A) Compound 2					
Te	0.10564(2)	0.00088(4)	0.38182(2)	4.707(6)	C6	0.2240(4)	0.4372(5)	0.5343(3)	4.9(1)
Cr	0.23832(5)	0.26453(7)	0.43548(4)	3.22(1)	C7	0.2036(4)	0.5083(5)	0.4521(3)	4.9(1)
O1	0.2533(3)	0.2437(5)	0.2444(2)	6.62(9)	C8	0.0963(4)	0.4443(5)	0.4048(3)	4.7(1)
O2	0.3619(3)	0.0171(4)	0.5537(2)	6.68(9)	C9	0.2285(4)	−0.1352(4)	0.3199(3)	3.78(9)
O3	0.5072(3)	0.3470(5)	0.4386(3)	7.4(1)	C10	0.1754(4)	−0.2415(6)	0.2604(3)	5.1(1)
C1	0.2458(4)	0.2452(5)	0.3172(3)	4.44(9)	C11	0.2492(5)	−0.3414(6)	0.2208(4)	6.5(1)
C2	0.3117(4)	0.1062(5)	0.5060(3)	4.36(9)	C12	0.3766(5)	−0.3332(6)	0.2412(4)	6.4(1)
C3	0.4048(4)	0.3147(5)	0.4369(3)	4.6(1)	C13	0.4307(4)	−0.2292(7)	0.3003(4)	6.5(1)
C4	0.0495(4)	0.3352(5)	0.4575(3)	4.41(9)	C14	0.3570(4)	−0.1294(6)	0.3398(3)	5.6(1)
C5	0.1287(4)	0.3311(5)	0.5367(3)	4.54(9)					
				(B) Compound 3					
Te1	0.20517(3)	0.41448(3)	0.38876(2)	2.803(5)	C12	0.4627(5)	0.6897(5)	0.2238(5)	4.8(1)
Te2	0.15633(3)	0.27230(2)	0.15277(2)	2.692(5)	C13	0.3568(6)	0.6324(5)	0.1395(4)	4.8(1)
Cr1	−0.04879(7)	0.30647(6)	0.26809(5)	2.95(1)	C14	0.2284(6)	0.6139(5)	0.1766(4)	4.6(1)
Cr2	0.35341(7)	0.49963(6)	0.24018(5)	2.87(1)	C15	0.2661(4)	0.2522(4)	0.4194(3)	3.09(9)
O1	−0.1344(4)	0.3921(4)	0.0808(3)	5.71(9)	C16	0.2208(5)	0.2102(5)	0.5066(4)	4.3(1)
O2	−0.0608(3)	0.5698(3)	0.3656(3)	4.59(8)	C17	0.2511(6)	0.1041(5)	0.5297(4)	5.2(1)
O3	0.5878(4)	0.4825(4)	0.3798(3)	6.5(1)	C18	0.3270(6)	0.0399(5)	0.4679(5)	5.4(1)
O4	0.5291(4)	0.3840(4)	0.1005(3)	6.8(1)	C19	0.3742(6)	0.0836(5)	0.3845(5)	5.2(1)
C1	−0.0970(4)	0.3589(4)	0.1515(4)	3.6(1)	C20	0.3452(5)	0.1896(5)	0.3602(4)	4.1(1)
C2	−0.0513(4)	0.4682(4)	0.3275(3)	3.39(9)	C21	0.0991(4)	0.2528(4)	−0.0092(3)	3.05(9)
C3	0.4927(5)	0.4885(5)	0.3282(4)	3.9(1)	C22	−0.0191(5)	0.1573(5)	−0.0592(4)	4.4(1)
C4	0.4560(5)	0.4237(5)	0.1520(4)	4.0(1)	C23	−0.0549(6)	0.1330(5)	−0.1647(4)	5.0(1)
C5	−0.1273(6)	0.2099(6)	0.3884(4)	5.7(1)	C24	0.0272(5)	0.2024(5)	−0.2224(4)	4.6(1)
C6	−0.2364(6)	0.2354(6)	0.3371(6)	7.1(2)	C25	0.1460(6)	0.2979(5)	−0.1745(4)	4.9(1)
C7	−0.2580(6)	0.1652(6)	0.2347(5)	6.5(2)	C26	0.1822(5)	0.3232(5)	−0.0677(4)	4.1(1)
C8	−0.1603(6)	0.0976(5)	0.2251(5)	5.2(1)	C27	0.4353(7)	−0.0597(6)	1.0712(6)	6.8(2)
C9	−0.0803(6)	0.1249(5)	0.3183(4)	4.7(1)	C28	0.3952(6)	0.0369(6)	1.0432(6)	6.4(2)
C10	0.2549(5)	0.6578(4)	0.2833(4)	4.6(1)	C29	0.4592(7)	0.0984(6)	0.9731(6)	6.6(2)
C11	0.3988(6)	0.7038(4)	0.3145(4)	4.6(1)					
				(C) Compound 4					
Te1	0.72142(5)	0.20257(2)	0.34660(5)	3.58(1)	C10	1.0124(9)	0.1007(5)	0.195(1)	6.4(3)
Te2	0.64335(6)	0.21193(3)	0.01075(6)	3.97(1)	C11	0.6979(8)	−0.0149(4)	0.2327(7)	3.4(2)
Te3	0.66035(5)	0.05429(2)	0.09075(5)	3.09(1)	C12	0.7612(9)	−0.0028(4)	0.3525(8)	4.8(2)
Cr1	0.5379(1)	0.14969(6)	0.1865(1)	3.02(3)	C13	0.787(1)	−0.0479(4)	0.4395(9)	5.9(3)
Cr2	0.8208(1)	0.14861(6)	0.1511(1)	2.96(3)	C14	0.7522(9)	−0.1080(4)	0.4105(9)	5.7(2)
C1	0.3307(8)	0.1609(5)	0.1043(9)	5.4(2)	C15	0.691(1)	−0.1214(4)	0.2953(9)	5.6(3)
C2	0.3518(8)	0.2038(4)	0.2010(9)	5.0(2)	C16	0.6601(9)	−0.0757(4)	0.2056(9)	4.8(2)
C3	0.3819(8)	0.1710(4)	0.3146(8)	4.5(2)	C17	0.7555(8)	0.1444(4)	0.5115(7)	3.8(2)
C4	0.3760(8)	0.1080(4)	0.2839(8)	4.4(2)	C18	0.652(1)	0.1181(5)	0.5667(9)	5.8(3)
C5	0.3428(8)	0.1015(4)	0.1546(8)	4.5(2)	C19	0.675(1)	0.0820(5)	0.6751(9)	6.4(3)
C6	1.0279(8)	0.1627(6)	0.2361(9)	6.8(3)	C20	0.7996(9)	0.0719(5)	0.7290(9)	5.9(3)
C7	1.0061(8)	0.1988(5)	0.129(1)	6.7(3)	C21	0.903(1)	0.0989(5)	0.6735(9)	5.9(3)
C8	0.9848(9)	0.1617(6)	0.028(1)	7.2(3)	C22	0.8812(9)	0.1351(5)	0.5656(8)	4.9(2)
C9	0.9865(9)	0.1036(5)	0.066(1)	6.4(3)					

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table 2. Bond Distances (Å) and Angles (deg) for 2

	(i) Coordination Geometry about Te Atom		
Te–Cr	2.7634(7)	Te–C9	2.117(4)
C9–Te–Cr	105.4(1)		
	(ii) Coordination Geometry about Cr Atom		
Cr–C1	1.857(5)	Cr–C2	1.859(5)
Cr–C3	1.851(5)	⟨Cr–Cp⟩	2.186(5)
O1–C1	1.147(5)	O2–C2	1.147(5)
O3–C3	1.140(5)		
Te–Cr–C1	74.2(1)	Te–Cr–C2	73.7(1)
C1–Cr–C2	115.8(2)	Te–Cr–C3	131.2(1)
C1–Cr–C3	81.0(2)	C2–Cr–C3	80.8(2)
Cr1–C1–O1	175.2(4)	Cr1–C2–O2	174.7(4)
Cr1–C3–O3	179.1(4)		
	(iii) Cyclopentadienyl and Phenyl Groups		
⟨C–C⟩$_{Cp}$	1.394(7)	⟨C–C⟩$_{Cp}$	1.374(7)
⟨C–C–C⟩$_{Cp}$	108.0(5)	⟨C–C–C⟩$_{Ph}$	120.0(5)

Experimental Section

General Considerations. All reactions were carried out either by use of conventional Schlenk techniques under nitrogen or under an argon atmosphere in a Vacuum Atmospheres Dribox equipped with a Model HE493 Dri-Train.

^{1}H and ^{13}C NMR spectra were measured on a JEOL FX100 100-MHz or JEOL GSX270 270-MHz spectrometer, and chemical shifts are referenced to residual C_6H_6 in benzene-d_6 or to $(CH_3)_4$-Si. IR spectra were measured in the range 4000–200 cm^{-1} by means of a JASCO IR Report-100 instrument. Elemental analyses were performed by the Analytical Unit of the Research School of Chemistry, Australian National University (for C, H of 2 and 3), Mikroanalytisches Labor Pascher, Remagen 2, Germany (for C, H, Cr, and Te of 4), and ourselves for other Cr analyses as CrO_4^{2-}.[19]

$[CpCr(CO)_3]_2$ was synthesized from $Cr(CO)_6$ (Strem Chemicals, Inc.) by the method of Manning *et al.*[20] Ph_2Te_2 (Strem Chemicals, Inc.) was used without purification. Silica gel (Merck Kieselgel 60, 35–70 mesh) and Florisil (Sigma Chemical Co., 100–200 mesh) were dried at 140 °C overnight before chromatographic use. All solvents used were distilled from sodium/benzophenone prior to use.

Reaction of $[CpCr(CO)_3]_2$ (1) with Ph_2Te_2. At Ambient Temperature. To a stirred green suspension of compound 1

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Table 3. Bond Distances (Å) and Angles (deg) for 3

(i) Coordination Geometry about Te Atom			
Te1–C15	2.151(4)	Te2–C21	2.138(4)
Te1–Te2	3.1371(4)		
Te1–C15–C16	116.1(3)	Te2–C21–C22	118.6(4)
Te1–C15–C20	124.8(4)	Te2–C21–C26	122.7(3)
Te2–Te1–Cr1	54.33(2)	Te1–Te2–Cr1	55.38(2)
Te2–Te1–Cr2	54.73(2)	Te1–Te2–Cr2	54.79(2)
Cr1–Te1–Cr2	97.67(2)	Cr1–Te2–Cr2	98.58(2)
(ii) Coordination Geometry about Cr Atom			
Cr1–C1	1.841(5)	Cr2–C3	1.810(5)
Cr1–C2	1.806(5)	Cr2–C4	1.831(5)
O1–C1	1.151(6)	O3–C3	1.163(6)
O2–C2	1.164(5)	O4–C4	1.147(6)
⟨Cr1–Cp⟩	2.193(6)	⟨Cr2–Cp⟩	2.197(5)
Te1–Cr1	2.7424(8)	Te2–Cr1	2.7070(7)
Te1–Cr2	2.7192(7)	Te2–Cr2	2.7175(7)
Cr1···Cr2	4.112(1)		
Te1–Cr1–Te2	70.29(2)	Te1–Cr2–Te2	70.48(2)
Te1–Cr1···Cr2	40.95(1)	Te1–Cr2···Cr1	41.38(1)
Te2–Cr1···Cr2	40.81(1)	Te2–Cr2···Cr1	40.62(1)
Cr1–C2–O1	176.0(4)	Cr2–C3–O3	175.6(5)
Cr1–C2–O2	176.2(4)	Cr2–C4–O4	174.7(5)
(iii) Cyclopentadienyl and Phenyl Groups			
$\langle C–C\rangle_{Cp1}$	1.38(1)	$\langle C–C\rangle_{Cp2}$	1.395(8)
$\langle C–C\rangle_{Ph1}$	1.375(8)	$\langle C–C\rangle_{Ph2}$	1.374(8)
$\langle C–C\rangle_{benzene}$	1.36(1)		
$\langle C–C–C\rangle_{Cp}$	108.0(6)	$\langle C–C–C\rangle_{Ph}$	120.0(6)

Table 4. Bond Distances (Å) and Angles (deg) for 4

(i) Coordination Geometry about Te Atom			
Te1–Te2	3.5814(9)	Te1–Te3	4.1953(8)
Te2–Te3	3.4950(8)	Te3–C11	2.13(1)
Te1–C17	2.15(2)		
Cr1–Te1–Cr2	67.06(4)	Te2–Te1–Te3	52.70(1)
Cr1–Te1–C17	108.6(3)	Cr2–Te1–C17	109.7(3)
Te2–Te1–Cr1	46.62(3)	Te2–Te1–Cr2	46.55(3)
Te3–Te1–Cr1	37.75(3)	Te3–Te1–Cr2	37.55(3)
Cr1–Te2–Cr2	68.47(4)	Te1–Te2–Te3	72.71(2)
Te1–Te2–Cr1	47.63(3)	Te1–Te2–Cr2	47.80(3)
Te3–Te2–Cr1	48.92(3)	Te3–Te2–Cr2	48.68(3)
Cr1–Te3–Cr2	67.34(4)	Te1–Te3–Te2	54.60(2)
Cr1–Te3–C11	109.2(3)	Cr2–Te3–C11	107.6(3)
Te1–Te3–Cr1	37.76(3)	Te1–Te3–Cr2	37.87(3)
Te2–Te3–Cr1	47.86(3)	Te2–Te3–Cr2	47.84(3)
(ii) Coordination Geometry about Cr Atom			
Cr1–Te1	2.653(1)	Cr2–Te1	2.661(1)
Cr1–Te2	2.610(1)	Cr2–Te2	2.608(1)
Cr1–Te3	2.653(1)	Cr2–Te3	2.642(1)
Cr1–Cr2	2.935(2)		
⟨Cr1–Cp1⟩	2.226(9)	Cr2–Cp2	2.22(1)
Te1–Cr1–Te2	85.76(4)	Te1–Cr2–Te2	85.64(4)
Te2–Cr1–Te3	83.22(4)	Te2–Cr2–Te3	83.48(4)
Te1–Cr1–Te3	104.49(5)	Te1–Cr2–Te3	104.59(5)
(iii) Cyclopentadienyl and Phenyl Groups			
$\langle C–C\rangle_{Cp1}$	1.39(1)	$\langle C–C\rangle_{Ph1}$	1.37(1)
$\langle C–C\rangle_{Cp2}$	1.36(2)	$\langle C–C\rangle_{Ph2}$	1.38(2)
$\langle C–C–C\rangle_{Cp1}$	108.0(9)	$\langle C–C–C\rangle_{Ph1}$	120(1)
$\langle C–C–C\rangle_{Cp2}$	108(1)	$\langle C–C–C\rangle_{Ph2}$	120(1)

(50 mg, 0.124 mmol) in toluene (10 cm^3) was added Ph_2Te_2 (50.9 mg, 0.124 mmol) at ambient temperature. A brownish green homogeneous solution was instantaneously formed. Stirring was continued for 2 h. The product solution was filtered through a Celite disk (*ca.* 1 cm thick), concentrated to *ca.* 1 mL, and loaded onto a silica gel column (1.5 cm × 7 cm) prepared in hexane. Elution gave three fractions. (i) A yellow solution in hexane (*ca.*

Table 5. Comparison of Selected Bond Distances (Å) and Angles (deg) for 2 with those for Its Se Analogue

	E = Te	E = Se[6]
E–Cr	2.7634(7)	2.588(1)
E–C9	2.117(4)	1.911(4)
Cr–E–C9	105.4(1)	109.6(1)
E–Cr–C1	74.2(1)	130.9(2)
E–Cr–C2	73.7(1)	73.8(1)
E–Cr–C3	131.2(1)	74.1(2)
C1–Cr–C2	115.8(2)	80.7(2)
C1–Cr–C3	81.0(2)	82.3(2)
C2–Cr–C3	80.8(2)	118.0(2)

Table 6. Comparison of Selected Bond Distances (Å) and Bond Angles (deg) for the Cr_2E_2 Core of 3 with Those for its S and Mo Analogues

	M = Cr, E = Te	M = Cr, E = S[5]	M = Mo, E = Te[18]
M1···M2	4.112(1)	3.808(2)	4.23
E1···E2	3.1371(4)	2.857(5)	3.24
M1–E1	2.7424(8)	2.449(3)	2.855(5), 2.874(6)
M1–E2	2.7070(7)	2.457(3)	2.785(5), 2.785(6)
M2–E1	2.7192(7)	2.471(3)	2.834(6), 2.834(6)
M2–E2	2.7175(7)	2.431(3)	2.813(5), 2.798(6)
E1–M1–E2	70.29(2)	71.2(1)	70.9(1), 69.3(2)
E1–M2–E2	70.48(2)	71.3(1)	70.8(1), 69.7(2)
M1–E1–M2	97.67(2)	101.4(1)	96.3(2), 95.3(2)
M1–E2–M2	98.58(2)	102.3(1)	98.4(2), 98.2(2)
E1–M1···M2	40.95(1)	39.5(1)	
E2–M1···M2	40.81(1)	38.6(1)	
E1–M2···M1	41.38(1)	39.1(1)	
E2–M2···M1	40.62(1)	39.1(1)	

50 cm^3) gave unreacted Ph_2Te_2 (12 mg, 0.029 mmol, 23.6%). (ii) A green solution in 1:1 hexane–toluene (*ca.* 25 cm^3) yielded green crystals of $CpCr(CO)_3(TePh)$ (**2**; 68 mg, 0.17 mmol, 67.2%). Anal. Calcd for $CpCr(CO)_3(TePh)$: C, 41.43; H, 2.49; Cr, 12.81%. Found: C, 41.44; H, 2.50; Cr, 12.06. ^1H NMR (C_6D_6): δ (Cp) varies from 3.98 (30 °C) to 4.18 (75 °C), $\delta(C_6H_5)$ 7.98, 7.95, and a multiplet with peaks at 7.02, 7.00, 6.97, 6.90, 6.87, 6.85. ^{13}C NMR ($CDCl_3$): δ(Cp) 89.57; $\delta(C_6H_5)$ 140.45, 128.36, and 127.87. IR (Nujol): ν(CO) 2050 vs, 1950 s, and 1935 s cm^{-1}; ν(Cp) 855 m cm^{-1}; ν(others) 740 m, 640 w, and 615 w cm^{-1}. IR (toluene): ν(CO) 1995 vs and 1930 vs cm^{-1}. FAB$^+$ mass spectrum: m/z 408 ([$CpCr(CO)_3(TePh)$]) and 324 ([CpCr(TePh)]). The electron impact spectrum shows m/z 410 ([$(TePh)_2$]), 282 ([$TePh_2$]), 207 ([TePh]), 201 ([$CpCr(CO)_3$]), 173 ([$CpCr(CO)_2$]), 145 ([CpCr(CO)]), and 117 ([CpCr]). (iii) A greenish brown solution in 3:7 *n*-hexane–toluene (*ca.* 10 cm^3) gave a 7:4 mixture (18 mg) of compound **2** and $[CpCr(CO)_2(TePh)]_2$ (**3**), described below.

At 60 °C. The brown product solution from a similar reaction after 4.5 h at 60 °C was worked up in a similar manner and chromatographed on a silica gel column (1.5 cm × 4 cm). Elution gave three fractions. (i) A yellow solution in hexane (*ca.* 40 cm^3) yielded unreacted Ph_2Te_2 (10 mg, 0.024 mmol, 19.6%). (ii) A green solution in 1:1 hexane–toluene (*ca.* 5 cm^3) gave green crystals of compound **2** (10 mg, 0.025 mmol, 10.1%). (iii) A brown solution in 1:1 hexane–toluene (*ca.* 30 cm^3) yielded brown crystals of compound **3** (75 mg, 0.099 mmol, 79.8%). Anal. Calcd for $[CpCr(CO)_2(TePh)]_2 \cdot {}^1/_2C_6H_6$: C, 43.83; H, 2.92; Cr, 13.02. Found: C, 43.85; H, 2.78; Cr, 13.52. ^1H NMR (C_6D_6): δ(Cp) varies from 4.41 (30 °C) to 4.47 (75 °C); $\delta(C_6H_5)$ 7.53, 7.51, and a multiplet with peaks at 7.06, 7.04, 7.01, 6.94, 6.92, and 6.89. ^{13}C NMR ($CDCl_3$): δ(Cp) 90.70; $\delta(C_6H_5)$ 137.40 and 128.36; δ(CO) 258.11 and 255.22. IR (Nujol): ν(CO) 1915 s, 1905 vs, 1860 s, and 1840 s cm^{-1}; ν(Cp) 820 m cm^{-1}; ν(others) 730 m, 690 m, and 630 m cm^{-1}. IR (toluene): ν(CO) 1935 s, 1920 vs, 1873 s, and 1860 s cm^{-1}. FAB$^+$ mass spectrum (see Figure 1A): m/z 756 ([$CpCr(CO)_2(TePh)]_2$), 700 ([$CpCr(CO)(TePh)]_2$), 644 ([$CpCr(TePh)]_2$), 567 ([$Cr_2Cp_2(Te_2Ph)$]), and 322 ([CpCr(TePh)]). The EI spectrum shows a very weak peak at m/z 756 and intense peaks at m/z 410 ([$(TePh)_2$]; see Figure 1C), 282 ([$(TePh_2)$]), and 207 ([TePh]).

Table 7. Data Collection and Processing Parameters

	2	3	4
molecular formula	$Cr(C_5H_5)(CO)_3(TeC_6H_5)$	$Cr_2(C_5H_5)_2(CO)_4(TeC_6H_5)_2\cdot{}^1/_2C_6H_6$	$Cr_2(C_5H_5)_2(TeC_6H_5)_2Te$
M_r	405.83	794.70	771.20
cryst color and habit	dark green parallelepipeds	magenta plates	dark green needles
cryst size (mm)	<0.3 in each dimens	0.3 × 0.2 × 0.2	0.3 × 0.3 × 0.3
unit cell params	a = 10.8250(8) Å, b = 8.6891(6) Å, c = 15.5263(7) Å, α = 90.009(4)°, β = 98.880(5)°, γ = 89.990(6)°, V = 1442.9(2) Å^3, Z = 4	a = 10.0493(8) Å, b = 11.0612(6) Å, c = 13.263(1) Å, α = 102.021(6)°, β = 93.791(7)°, γ = 105.652(5)°, V = 1376.7(2) Å^3, Z = 2	a = 10.1595(7) Å, b = 21.505(1) Å, c = 10.615(1) Å, α = 90°, β = 95.607(8)°, γ = 90°, Z = 4
D_{calc} (Mg m^{-3})	1.868	1.917	2.219
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
radiation (Å)	Mo Kα (λ = 0.710 73)	Mo Kα (λ = 0.710 73)	Mo Kα (λ = 0.710 73)
no. of rflns for lattice params	25	21	25
θ range for lattice params (deg)	14–16	13–16	12–15
abs coeff (cm^{-1})	27.61	28.87	46.5
temp (°C)	27	27	27
diffractometer type	CAD4	CAD4	CAD4
collection method	ω–2θ	ω–2θ	ω–2θ
abs cor (T_{min}, T_{max})	86.008, 99.822	88.154, 99.956	91.94, 99.91
no. of rflns measd	2866	4515	4413
no. of indep rflns	2527	4338	4049
θ_{max} (deg)	25	25	25
no. of obsd rflns (>3$\sigma(I)$)	1857	3346	2539
no. of std rflns (and interval)	3(400)	3(400)	3(400)
variation of stds (% h^{-1})	-4.91×10^{-2}	-1.49×10^{-1}	−1.03
collection range	h = 0–12, k = −10 to 0, l = −18 to +18	h = −11 to +11, k = −13 to 12, l = 0–15	h = −12 to +12, k = 0–25, l = 0–12
R	0.023	0.022	0.030
R_w	0.025	0.024	0.035
weighting scheme	$w = [\sigma^2(F) + 0.0004F^2 + 1]^{-1}$	$w = [\sigma^2(F) + 0.0004F^2 + 1]^{-1}$	$w = [\sigma(F)^2]^{-1}$
no. of params refined	212	426	244
no. of rflns used in refinement	1857	3346	2539
S	0.349	0.329	1.026
$(\Delta/\sigma)_{max}$	0.29	0.38	0.00
$(\Delta\rho)_{max}$ (e Å^{-3})	0.672	0.432	0.627

At 80 °C. The dark green product solution from a similar reaction for 4 h at 80 °C upon similar workup and chromatography gave (i) a brown eluate in 1:1 hexane–toluene (*ca.* 25 cm^3), which yielded brown crystals of compound **3** (28 mg, 0.037 mmol, 29.8%), and (ii) a turquoise green eluate in 2:5 hexane–toluene, which gave dark green crystals (39 mg, 0.051 mmol, 40.8%) of the compound $[CpCr(TePh)]_2Te$ (**4**). Anal. Calcd for $[CpCr(TePh)]_2Te$: C, 34.26; H, 2.61; Cr, 13.48; Te, 49.64. Found: C, 33.94, 33.76; H, 2.62, 2.68; Cr, 13.11, 13.2; Te, 49.1. ^{1}H NMR (C_6D_6) at ambient temperature: δ(Cp) 15.82 ($\nu_{1/2}$ = 35 Hz) and 19.80 ($\nu_{1/2}$ = 20 Hz) with relative intensity *ca.* 1:1 $\delta(C_6H_5)$ multiplet with peaks at 9.14, 8.97, 8.34, 8.13, 7.68, 7.60, 7.40, 7.33, 6.87, 6.85, and 6.82 (total *ca.* 10 H, integration accuracy affected by solvent peaks). VT ^{1}H NMR ($C_6D_5CD_3$) of a sample prepared by dissolution at *ca.* 90 °C and scanned initially at −90 °C followed by stepwise increases in temperature to 80 °C: −90 °C, δ (Cp) 9.50 ($\nu_{1/2}$ = 40 Hz) and 13.27 ($\nu_{1/2}$ = 20 Hz) (relative intensity *ca.* 1:1); 80 °C, δ(Cp) 17.41 ($\nu_{1/2}$ = 30 Hz) and 21.04 ($\nu_{1/2}$ = 30 Hz) (relative intensity *ca.* 1:1). IR (Nujol): ν 800 m, 715 s, and 690 w cm^{-1}. ^{13}C NMR (C_6D_6): δ(Cp) 97.3 (br); $\delta(C_6H_5)$ 137.79, 135.76, 135.21, 134.20, 129.99, and 126.17 (partially obscured by solvent peaks). The only significant fragments in both the EI and FAB$^+$ mass spectra of **4** are m/z 410 ($[(TePh)_2]$), 282 ($[TePh_2]$), 207 ([PhTe]), 154 ($[Ph_2]$).

Reaction of $[CpCr(Co)_2]_2$ with Ph_2Te_2: An NMR Study. A solution in C_6D_6, 20 mM each in $[CpCr(CO)_2]_2$ and Ph_2Te_2, was maintained at *ca.* 70 °C in a 5 mm serum-capped NMR tube, vented into a nitrogen line, and its proton NMR spectrum monitored at intervals.

Thermolysis Reactions. An approximately 10 mM green solution of compound **2** and a 2 mM brown solution of compound **3** in C_6D_6 in 5-mm NMR tubes were maintained at 80 °C, and the progress of their thermolytic degradation was monitored via their proton NMR spectra. The decay of **2** was also monitored at 60 °C.

Crystal Structure Determination. Dark green parallelepipeds of compound **2** were obtained from toluene–hexane after 1 day at −20 °C. Complex **3** was obtained as dark magenta-brown plates from toluene–ether after 2 days at ambient temperature. Deep green crystals of **4** were obtained from toluene–hexane after several weeks at −20 °C.

Diffraction-quality crystals were coated with epoxy glue to prevent crystal decomposition. Details of the crystal parameters, data collection, and structure refinement are given in Table 7. Raw intensities collected at room temperature were processed for Lorentz–polarization effects and corrected for absorption using ψ-scan data.[21] The Patterson method yielded the positions of the Te atoms for **2** and **3**, and the rest of the atoms were derived from successive difference Fourier syntheses. Compound **4** was solved by MULTAN. The non-hydrogen atoms were subjected to anisotropic refinement, while the H atoms for **2** and **3** were refined isotropically. The H atoms for **4** were generated geometrically and were allowed to ride on their parent carbon atoms with B fixed at 1.3 times those of the parent C atoms. Computations were performed using the MolEN[22] package on a DEC MicroVAX-II computer. Analytic expressions of atomic

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scattering factors[23] were employed, and anomalous dispersion-corrections[24] were incorporated. Anisotropic displacement parameters, hydrogen atom coordinates, and structure factor tables have been deposited with the Cambridge Crystallographic Data Centre.

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Supplementary Material Available: Tables of anisotropic displacement parameters and additional bond distances and angles for **2–4** and of positional parameters for the hydrogen atoms of **2** and **3** (8 pages). Ordering information is given on any current masthead page.

OM930606E

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