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Reactions of μ-Alkylidyne Complexes with Tellurium. Telluroacyl versus μ-Telluride Formation

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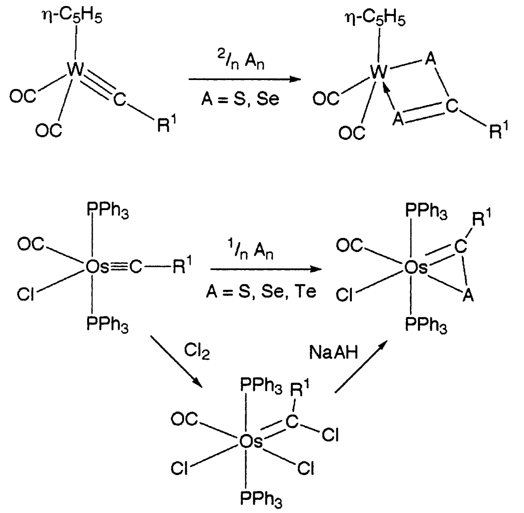
The reactions of heterobimetallic μ-alkylidyne complexes [MFe(μ-CR)(CO)$_n$(η-C$_5$H$_5$)] (M = W, Mo; R = C_6H_4Me-4 (R^1), $C_6H_3Me_2$-2,6 (R^2); n = 5, 6) with elemental tellurium are reported. For [WFe(μ-CR^1)(CO)$_n$(η-C$_5$H$_5$)] (n = 5 or 6), the only isolated product is the first example of a complex with a bridging telluroaroyl ligand [WFe(μ-TeCR^1)(CO)$_5$(η-C$_5$H$_5$)] (**5a-Te**), which reacts with dppm to provide [WFe(μ-TeCR^1)(μ-dppm)(CO)$_3$(η-C$_5$H$_5$)] (**6-Te**). The complexes [MFe(μ-CR^2)(CO)$_5$(η-C$_5$H$_5$)] (M = W, Mo) however react with tellurium under ultrasonic activation to provide the telluroaroyl [MoFe(μ-TeCR^2)(CO)$_5$(η-C$_5$H$_5$)] (**5b-Te**) or μ-telluride clusters [MFe$_2$(μ-CR^2)(μ_3-Te)(CO)$_7$(η-C$_5$H$_5$)] (M = W **7a-Te**, M = Mo **7b-Te**). Complex **7a-Te** reacts with dppm to provide [MFe$_2$(μ-CR^2)(μ_3-Te)(CO)$_7$(η-C$_5$H$_5$)] (**8b-Te**). Crystal structures of **5a-Te**, **6a-Te**, and **7a-Te** are reported.

Introduction

We have previously described the synthesis and reactivity of a range of thioaroyl complexes of tungsten and molybdenum that arise from reactions of methylthiirane with alkylidyne complexes.[1] The choice of methylthiirane as a single atom sulfur transfer reagent appears crucial since elemental sulfur[2] or cyclohexene episulfide[3] transfer two atom equivalents to provide dithiocarboxylate complexes. In a similar manner, elemental selenium reacts with alkylidyne complexes [M(≡CR)L$_2$(η-C$_5$H$_5$)] (M = W, L = CO, R = C_6H_4Me-4; M = Mo, L = P(OMe)$_3$, R = CH_2CMe_3) to provide diselenocarboxylate complexes [M(κ^2-Se$_2$CR)L$_2$(η-C$_5$H$_5$)],[2a] while the related alkylidyne complex [Mo(≡CC$_6$H$_4$OMe-4)(CO)$_2${HB(pz)$_3$}] (pz = pyrazol-1-yl) fails to react with elemental tellurium.[1] Thus within group 6 there exist at present no synthetic routes to mononuclear complexes of seleno- or telluroacyl ligands. This observation contrasts with the chemistry of group 8, wherein the first (and still only) complete series of chalcoaroyls [Os(η^2-ACC$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] (A = S, Se, Te) has been obtained from reactions of (i) the toluidyne complex [Os(≡CC$_6$H$_4$Me-4)Cl(CO)(PPh$_3$)$_2$] with elemental chalcogens or (ii) the chlorotoluidene complex [OsCl$_2$(=CClC$_6$H$_4$-Me-4)(CO)(PPh$_3$)$_2$] with hydrochalcogenide (Scheme 1).[4]

Scheme 1. Reactions of Toluidyne Complexes with Chalcogens (R^1 = C$_6$H$_4$Me-4)[2a,4]



This latter route is mirrored in the synthesis of the first complete series of chalcocarbamoyl complexes [Ru(η^2-ACNMe$_2$)Cl(CO)(PPh$_3$)$_2$] that result from similar treatment of a chloroaminocarbene complex [RuCl$_2$(=CClNMe$_2$)(CO)(PPh$_3$)$_2$].[5] After two decades, these series include the only examples of telluroacyl ligands. A small number of telluroaldehyde complexes have been reported,[6] which in general arise from addition of tellurium to alkylidene[7] or vinylidene[8] complexes, nu-

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cleophilic attack by hydrotelluride at haloalkyl ligands,[9] or reactions of telluride complexes with diazoalkanes.[10]

The lack of development of transition metal chemistry of unsaturated organotellurium ligands, by comparison with that of sulfur and selenium, may be traced to a number of factors that make it more challenging. The "double-bond rule" retains considerable sway over multiple bonding between carbon and tellurium. Furthermore, C−Te single bonds are characteristically weak. Thus there is a dearth of suitable unsaturated organotellurium precursors for study.[11−15] The alternative approach, i.e., construction of unsaturated organotellurium ligands within the protective environment of a coordination sphere, has met with some success (vide supra).[6−10,14] The addition of elemental tellurium across metal−carbon multiple bonds is attractive; however it is hampered by the insolubility of elemental tellurium and the possible reversibility, i.e., extrusion of tellurium to (re)generate a metal−carbon multiple bond. This latter point is illustrated by the instability of the complex $[\mathrm{Os}(\eta^2\text{-TeC{=}S})\mathrm{Cl(NO)(PPh_3)_2}]$, which under ambient conditions provides the thiocarbonyl complex $[\mathrm{OsCl(NO)(CS)(PPh_3)_2}]$,[16] contrasting with the addition of tellurium to $[\mathrm{OsCl(NO)({=}CH_2)(PPh_3)_2}]$ to provide $[\mathrm{OsCl(NO)}(\eta^2\text{-Te{=}CH_2})\mathrm{(PPh_3)_2}]$[7a] (Scheme 2).

Scheme 2. Tellurium Addition/Extrusion Reactions[7a,16]

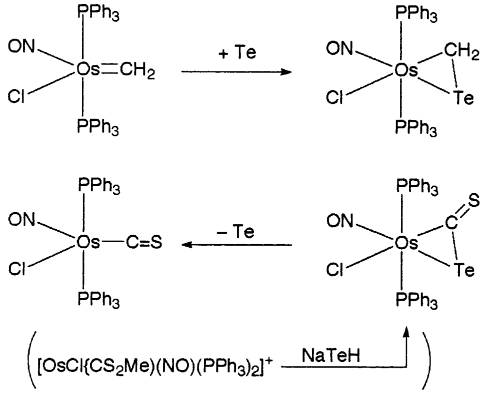
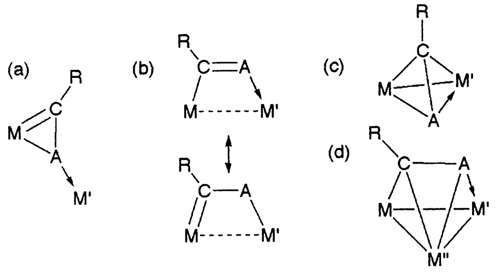


Chart 1. Possible Bridging Coordination Modes for Chalcoacyls and Carbamoyls (RCA: A = S, Se, Te) with Valence Electron Counts: (a) 5VE (3,2); (b) Parallel, 3VE (1,2↔2,1); (c) Transverse, 5VE (2,3); (d) μ_3, 5VE (1,2,2).



Otherwise unstable and/or highly reactive small molecules may occasionally be better stabilized through coordination to bi- and polymetallic ensembles than within mononuclear complexes. Accordingly, we have turned our attention to the synthesis of binuclear complexes of telluroacyl ligands, building on previous work that suggests a particular stability for coordination of thioaroyl, thioacyl, and thiocarbamoyl[17−22] ligands across metal−metal bonds, wherein the ligand can provide up to five electrons to the valence count (Chart 1). Herein, we report the reactions of alkylidyne-bridged bimetallic complexes $[\mathrm{MFe}(\mu\text{-CR})(\mathrm{CO})_n(\eta\text{-C_5H_5})]$ (M = W, Mo; $n = 5$ (**3**), 6 (**2**); R = R^1, R^2; hereafter R^1 = $\mathrm{C_6H_4Me}$-4, R^2 = $\mathrm{C_6H_3Me_2}$-2,6) with elemental tellurium to provide the first bimetallic telluroacyl complexes.

Results and Discussion

The complex $[\mathrm{W}(\equiv\mathrm{CR^1})(\mathrm{CO})_2(\eta\text{-C_5H_5})]$ (**1a**, Chart 2) has been shown to react with $[\mathrm{Fe_2(CO)_9}]$ to provide the 34-valence-electron bimetallic complex $[\mathrm{WFe}(\mu\text{-CR^1})(\mathrm{CO})_6(\eta\text{-C_5H_5})]$ (**2a**), albeit in low yield (10%) due to

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[11] Telluroaldehydes have not been isolated, although their intermediacy follows from trapping experiments;[12] telluroketones have been isolated by employing sterically demanding substituents,[13] and complexes of carbon monotelluride have been prepared by constructing the CTe ligand within a coordination sphere.[14] Telluroureas and amides have also been isolated, for which zwitterionic resonance forms with reduced C−Te multiple bonding seem appropriate.[15]

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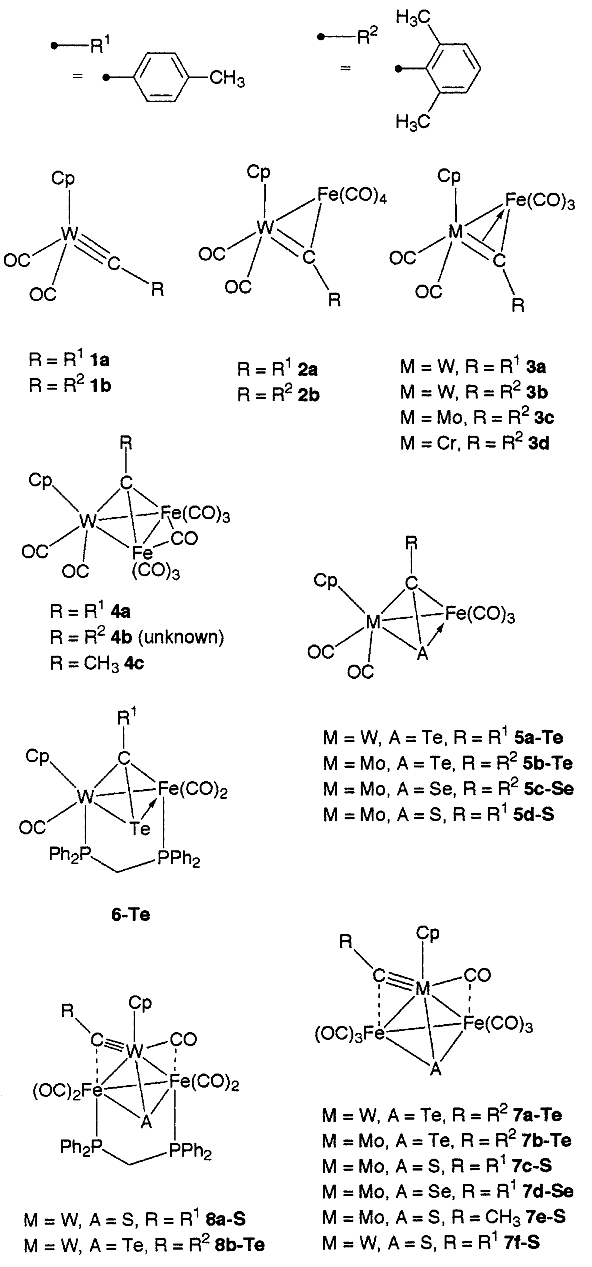
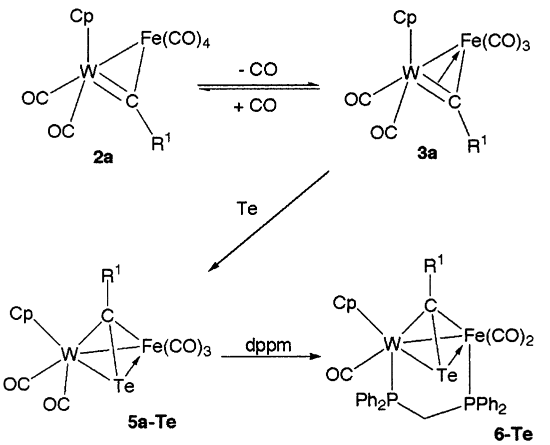
Chart 2. Generic Structural Motifs



Scheme 3. Binuclear Tellurotoluoyl Complexes (R^1 = C$_6$H$_4$Me-4)



subsequent reactions with either [Fe$_2$(CO)$_9$] or **1a** to provide [WFe$_2$(μ_3-CR^1)(CO)$_9$(η-C$_5$H$_5$)] (**4a**) or [W$_2$Fe(μ-R^{1}CCR^1)(CO)$_6$(η-C$_5$H$_5$)$_2$], respectively.[23] In contrast, the 32-valence-electron complex [WFe(μ-CR^2)(CO)$_5$(η-C$_5$H$_5$)] (**3b**) is readily isolated from the corresponding reaction of [W(≡CR^2)(CO)$_2$(η-C$_5$H$_5$)] (**1b**) with [Fe$_2$(CO)$_9$] without formation of trimetallic products.[24] Indeed, the 34VE complex [WFe(μ-CR^2)(CO)$_6$(η-C$_5$H$_5$)] (**2b**) is only spectroscopically observable in situ under a CO atmosphere. We now find that reasonable yields of **2a** (38%) and traces (5%) of [WFe(μ-CR^1)(CO)$_5$(η-C$_5$H$_5$)] (**3a**) can be obtained if the reaction vessel is periodically evacuated and the resulting mixture chromatographed at −30 °C. With useful quantities of these materials in hand, the reactions with elemental tellurium were investigated and found to provide a new telluroacyl complex, [WFe(μ-TeCR^1)(CO)$_5$(η-C$_5$H$_5$)] (**5a-Te**). Notably, the reaction of **3a** is complete within 5 min, while the reaction of **2a** requires 1 h to proceed to completion, suggesting that even for **2a**, dissociation of CO (to provide **3a**) is a prerequisite. Although the exact sulfur and selenium analogues of **5a-Te** based on tungsten have yet to be reported, close relatives are known wherein more sterically demanding groups replace either the alkylidyne substituent (C$_6$H$_3$Me$_2$-2,6)[17b] or the cyclopentadienyl ligand (η-C$_5$Me$_5$,[25] HB(pz)$_3$, pz = pyrazol-1-yl[26]) or both.[2b] Thus the formulation of **5a-Te** rests firmly on FAB-MS and spectroscopic data which conform to precedents for thioaroyl and selenoaroyl analogues. Specifically, the infrared spectrum of **5a-Te** includes a set of five CO-related absorbances with an intensity profile comparable to those of the sulfur and selenium analogues. The carbonyl ligands are also manifest in the ^{13}C{^{1}H} NMR spectrum as three peaks at 214.4, 210.6, and 210.2 ppm corresponding to one carbonyl ligand with semibridging character, the Fe(CO)$_3$ group, and the terminal tungsten carbonyl ligand, respectively. The semibridging role of one carbonyl is also suggested by the low value of one weak IR absorption at 1860 cm^{-1}. The telluroacyl carbon gives rise to a resonance at 172.7 ppm which is shifted to far lower field of the region associated with bridging thio- and selenoacyl ligands (Table 1). Suitable data for comparison are somewhat sparse, and it would be premature to attempt to generalize; however it can be noted that, of all the chalcogens, tellurium is the most "metallic" in nature. Accordingly, it might be supposed that the telluroaroyl carbon is in some ways more akin to a μ_3-alkylidyne (typically δ_C = 250−320 ppm). From this perspective, one might expect a substantial downfield shift. Notably, the series [OsCl$_2$(CO)(CA)(PPh$_3$)$_2$] shows a sequential downfield shift in δ_{CA} for heavier chalcogens [A = O (172.9), S (258.7), Se (278.8) Te (297.7 ppm)].[14b] The molecular structure of **5a-Te** was confirmed by a single-crystal X-ray diffraction study, the results of which are summarized in Figure 1 and discussed below.

The 32VE complexes [MFe(μ-CR^2)(CO)$_5$(η-C$_5$H$_5$)] (M = W **3b**, Mo **3c**) were found not to react with elemental

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Table 1. ^{13}C NMR Data for Bridging Chalcoacyl Complexes

complex				$\delta(^{13}CA)$	reference
$[MFe(\mu\text{-}ACR)(CO)_5(L)]$ (**5**)					
M	R	A	L		
Cr	R^2	S	C_5H_5	112.6	17a
Mo	R^1	S	C_5H_5	111.3[a]	17a
Mo	R^1	S	$HB(pz)_3$	106.0	1a, 23
Mo	R^2	Se	C_5H_5	126.5	17b
Mo	R^2	Te	C_5H_5	163.0	
W	R^1	S	C_5Me_5	95.6	22
W	R^2	S	C_5H_5	127.6	17b
W	R^2	Se	C_5H_5	112.9	17b
W	R^1	Te	C_5H_5	172.7	
$WFe_2(\mu\text{-}SCMe)(CO)_8(\eta\text{-}C_5H_5)$				174.3[b]	27
$WFe(\mu\text{-}TeCR^1)(CO)_3(dppm)(\eta\text{-}C_5H_5)$				178.5[a]	
$Fe_2(\mu\text{-}SCCyMe_4)(CO)_4(NO)(PPh_3)$				136.7[a]	18d
$[Fe_2(\mu\text{-}SCCyMe_4)(CO)_6]^-$				108.8[a]	18d
$W_2Re(\mu\text{-}SCR^1)(\mu\text{-}CR^1)(\mu\text{-}Br)(CO)_4(\eta\text{-}C_5H_5)_2$				90.0	19

[a] Structurally characterized. [b] Mode d, Chart 1

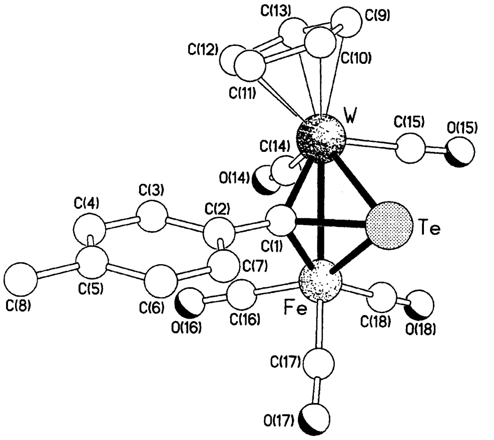

Figure 1. Molecular structure of **5a-Te**.

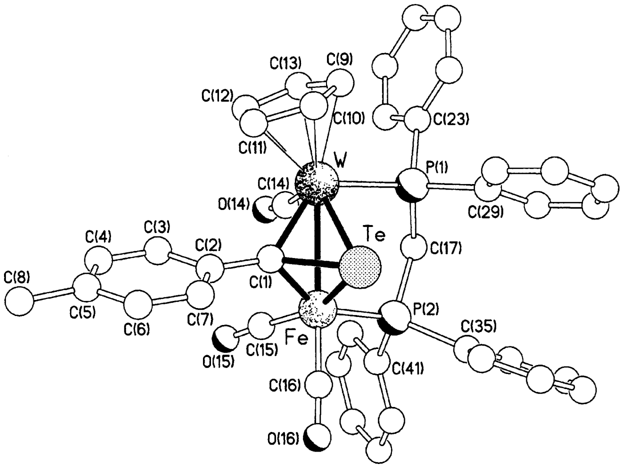

Figure 2. Molecular structure of **6-Te**.

tellurium under ambient conditions, in contrast with reactions of these complexes with selenium, which proceed to completion within 15 h.[17b] This we attribute primarily to the poor solubility of elemental tellurium since under the same conditions but with ultrasonolysis brown solutions are obtained after 1 h (Mo) or 8 h (W). Although accompanied by considerable decomposition, in the case of tungsten the major compound was identified as the trimetallic cluster $[WFe_2(\mu\text{-}CR^2)(\mu_3\text{-}Te)(CO)_7(\eta\text{-}C_5H_5)]$ (**7a-Te**) arising from disproportionation of the starting complex. One notable feature of both the ^1H and $^{13}C\{^1H\}$ NMR spectra for **5a-Te** is that the xylyl methyl substituents are chemically inequivalent, indicating that this group does not freely rotate on the NMR time scale(s). The crude reaction mixture obtained in the case of molybdenum had spectroscopic data consistent with the presence of both $[MoFe_2(\mu\text{-}CR^2)(\mu_3\text{-}Te)(CO)_7(\eta\text{-}C_5H_5)]$ (**7b-Te**) and $[MoFe(\mu\text{-}TeCR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (**5b-Te**). A “pure” mixture of these two compounds could be obtained by chromatography at −40 °C, while flash chromatography at room temperature led only to the isolation of pure **5b-Te** in trace amounts, with **7b-Te** remaining bound to the silica gel. Spectroscopic data for **5b-Te** are directly comparable to those for **5a-Te**, including the appearance of a ^{13}C resonance at 163.0 ppm attributable to the telluroaroyl carbon (δ_{CTe}) and once again shifted downfield from the corresponding selenium analogue $[MoFe(\mu\text{-}SeCR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (**5c-Se**: $\delta_{CSe} = 126.5$).[17b]

The cluster **7a-Te** is analogous to those obtained from reactions of $[WFe_2(\mu\text{-}CR)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ ($R = R^1$ **4a**, CH_3 **4c**) with either sulfur or selenium.[27] One example of these, $[WFe_2(\mu\text{-}CR^1)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)]$ (**7f-S**), has been structurally characterized, and accordingly the crystal structure of **7a-Te** was determined for comparison. The results of this study are summarized in Figure 2 and discussed below. The spectroscopic data for **7a-Te** are essentially comparable with those for the clusters $[MoFe_2(\mu\text{-}CR^1)(\mu\text{-}A)(CO)_7(\eta\text{-}C_5H_5)]$ (A = S **7c-S**, Se **7d-Se**):[25] The bridging alkylidyne gives rise to a $^{13}C\{^1H\}$ resonance at 319.1 ppm, which is almost identical to that for **7d-Se** ($\delta_C = 318.5$) and shifted downfield from that for **7c-S** ($\delta_C = 285.9$). The semibridging nature of one carbonyl ligand in each of the complexes **7c-S** and **7d-Se** is reflected in the $^{13}C\{^1H\}$ NMR data (**7c-S**: 241.8; **7d-Se**: 244.2 ppm), and in the case of **6c** this was confirmed crystallographically.[25] For **7a-Te** however, this is less definitive with δ_{WFeCO} at 237.5 ppm; however this was confirmed in the solid state (vide infra). ^1H and $^{13}C\{^1H\}$ NMR data indicate that the bulky alkylidyne group does not freely rotate on the NMR time scale(s).

The formation of the trimetallic complex **7a-Te** from the dimetallic precursor calls for comment, in that trimetallics were not encountered in the corresponding

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reactions of $[MFe(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(CO)_5(\eta\text{-}C_5H_5)]$ (M = W (**3b**), Mo (**3c**), W (**3d**)) with selenium or sulfur, each of which proceeded cleanly to binuclear heteroaroyl complexes.[17b] While use of ultrasonolysis to activate the tellurium may be harsh, mild ultrasound (cleaning bath) in general does not lead to different product distributions in homogeneous media other than activation of heterogeneous interfaces.[28] Thus we suspect that formation of **7a-Te** reflects the established preference of 2,6-disubstituted benzylidyne ligands for adopting μ_2-bridging (i.e., sp^2-C) over μ_3-bridging (i.e., sp^3-C) geometries, thereby alleviating steric conflicts. Notably, the cluster $[WFe_2(\mu_3\text{-}CR^2)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**4b**) remains unknown for just this reason and may reasonably be excluded as an intermediate in the formation of **7a-Te**, though the isolable toluidyne example $[MoFe_2(\mu_3\text{-}CR^1)(\mu\text{-}CO)(CO)_8(\eta\text{-}C_5H_5)]$ (**4a**) has been shown to react with sulfur to provide a mixture of the clusters **7f-S** and $[MoFe_2(\mu\text{-}SCR^1)(CO)_8(\eta\text{-}C_5H_5)]$.[17a] We therefore suggest that the bimetallic complex "$[WFe(\mu\text{-}TeCR^2)(CO)_5(\eta\text{-}C_5H_5)]$" is formed first, but under these conditions disproportionates to generate **7a-Te** by trapping of liberated iron carbonyl fragments and subsequent cleavage of the C−Te bond. In support of this contention, Stone has demonstrated that C−S cleavage of a thioacyl ligand can be facile on the trimetallic cluster $[WFe_2(\mu_3\text{-}SCMe)(\mu\text{-}CO)_2(CO)_6(\eta\text{-}C_5H_5)]$ to provide $[MoFe_2(\mu\text{-}CMe)(\mu\text{-}S)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$ (**7e-S**).[27] Given the comparative weakness of C−Te versus C−S bonds, it seems reasonable that such a cleavage to regenerate the alkylidyne ligand would be correspondingly more facile. The presumed fragility of "$[WFe(\mu\text{-}TeCR^2)(CO)_5(\eta\text{-}C_5H_5)]$" under these conditions is also consistent with the low isolated yields of $[MoFe(\mu\text{-}TeCR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (**5b-Te**) obtained under these conditions.

The complexes $[MFe(\mu\text{-}ACR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (**5**, M = Cr, Mo, W; A = S, Se) undergo CO substitution reactions with bis(diphenylphosphino)methane (dppm) in refluxing toluene to provide $[MFe(\mu\text{-}ACR^2)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)]$, which may alternatively be obtained by addition of sulfur to the complex $[MFe(\mu\text{-}CR^2)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)]$, again in refluxing toluene.[17b] In a similar manner, heating **5a-Te** with dppm in benzene under reflux provided modest yields (57%) of the diphosphine-bridged complex $[WFe(\mu\text{-}TeCR^1)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)]$ (**6-Te**). Spectroscopic data for **6-Te** are similar to those for the corresponding selenoaroyl complex $[WFe(\mu\text{-}SeCR^2)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)]$[17b] with the exception that once again the $^{13}C\{^1H\}$ resonance for the telluroaroyl carbon is shifted to low field (δ_{CTe} 178.5), showing coupling to the two phosphorus nuclei (dd: $^2J_{PC}$ = 25 and 37 Hz). In the case of the selenoaroyl analogue, δ_{CSe} was not unambiguously distinguished from aryl resonances. That the dppm ligand adopts a bridging rather than chelating role is indicated by the appearance of satellites due to $^{183}W^{31}P$ coupling ($^1J_{WP}$ = 272 Hz) evident for *one* of the resonances in the $^{31}P\{^1H\}$ NMR spectrum of **6-Te**. This was confirmed by a crystal structure determination, the results of which are summarized in Figure 3 and discussed below. The cluster $[WFe_2(\mu\text{-}CR^1)(\mu\text{-}S)(\mu\text{-}dppm)(CO)_5(\eta\text{-}C_5H_5)]$ (**8a-S**) has been found to arise from reaction of sulfur with $[WFe_2(\mu_3\text{-}CR^1)(\mu\text{-}dppm)(CO)_7(\eta\text{-}C_5H_5)]$, a precursor that already has the dppm ligand bridging the Fe−Fe bond.[27] A similar cluster, $[WFe_2(\mu\text{-}CR^2)(\mu\text{-}Te)(\mu\text{-}dppm)(CO)_5(\eta\text{-}C_5H_5)]$ (**8b-Te**), is obtained from reaction of **7a-Te** with dppm in refluxing benzene. The reaction is however accompanied by re-formation of significant amounts of $[W(\equiv CR^2)(CO)_2(\eta\text{-}C_5H_5)]$ (**1b**) in a cluster degradation process, even though the conditions (ca. 80 °C) are somewhat milder than those for the formation of **8a-S** (ca. 110 °C). The $^{31}P\{^1H\}$ NMR spectrum of **8b-Te** comprises an AB pattern (δ_A = 59.5 δ_B = 63.7, $^{2,3}J_{AB}$ = 76 Hz), each resonance of which displays ^{183}W satellites. Notably, the magnitudes of these are quite different, such that $^2J_{AW}$ = 98 while $^2J_{BW}$ = 45 Hz. The former is considerably smaller than $^1J_{WP}$ observed for **6a-Te**, wherein one phosphorus is directly bound to tungsten. Thus, assuming that the dppm does indeed bridge the Fe−Fe and not the W−Fe bond, the disparity in WP couplings must arise from an enhancement of coupling by the bridging carbyne carbon, since the crystal structure of **7a-Te** (vide infra) shows that the alkylidyne bridge does not significantly contract the W−Fe bond relative to that devoid of a bridge other than the μ_3-telluride.

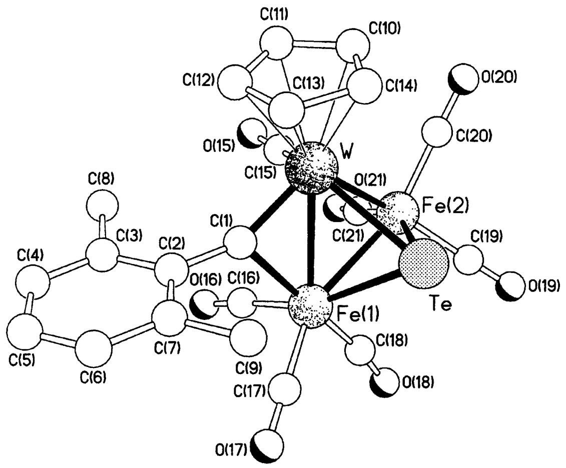
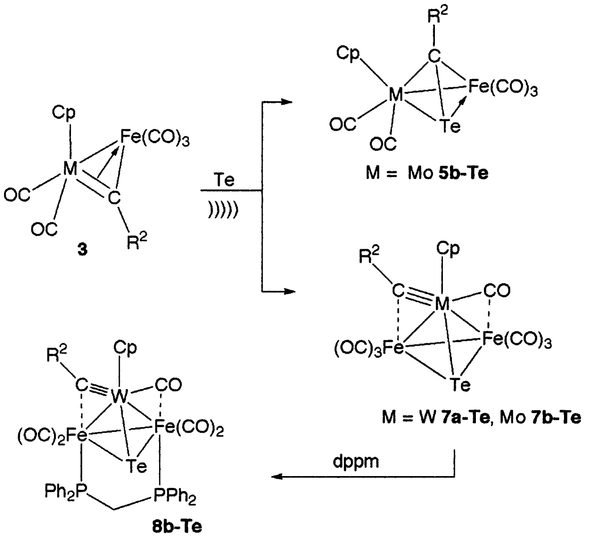


Figure 3. Molecular structure of **7a-Te**.

Scheme 4. Telluroaroyl versus Telluride Formation ($R^2 = C_6H_3Me_2$-2,6)



Molecular Structure of $[WFe(\mu\text{-}TeCR^1)(CO)_5(\eta\text{-}C_5H_5)]$ (5a-Te). Figure 1 displays the molecular geometry of **5a-Te** in the crystal. Comparative structural

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(28) Suslick, K. S. *Adv. Organomet. Chem.* **1986**, *25*, 73.

Table 2. Comparison of Geometric Parameters (Å, deg) for the Complexes [$MFe(\mu\text{-}ACR^1)(CO)_3(\eta\text{-}C_5H_5)L_2$]

	M, A, L_2 =		
	W, Te, $(CO)_2$ (**5a-Te**)	W, Te, μ-dppm (**6-Te**)	Mo, S, $(CO)_2$ (**5d-S**)[17a]
M−Fe	2.7844(7)	2.7741(15)	2.765(1)
M−A	2.7687(5)	2.7659(10)	2.441(1)
M−C(1)	2.127(5)	2.124(10)	2.153(2)
Fe−A	2.5717(8)	2.5786(17)	2.248(1)
Fe−C(1)	1.937(5)	1.966(10)	1.942(2)
C(1)−A	2.136(4)	2.148(8)	1.735(2)

data are not available for bridging telluroacyl[30] or selenoacyl complexes.[31] Accordingly, the complex [$MoFe(\mu\text{-}SCR^1)(CO)_5(\eta\text{-}C_5H_5)$] (**5d-S**)[17a] provides the best basis for interpreting the structure of **5a-Te**, on the assumption that Mo and W have comparable covalent radii (Table 2). The cyclopentadienyl and carbonyl ligands in **5a-Te** are unremarkable other than to note that as in the case of **5d-S**, one displays mild semibridging character with an Fe−C(14) separation of 2.781(5) Å. The tolyl substituent appears to adopt an orientation so as to minimize steric conflict with the cyclopentadienyl, tellurium, and carbonyl ligands. The features of interest, however, relate to the C(1)FeWTe core, which is comprised of an Fe−W bond of 2.7844(7) Å (cf 2.765(1) Å in **5d-S**) traversed in an essentially orthogonal manner by the C(1)−Te bond [W−Fe and C(1)−Te vectors inclined by 88.7(2)°], which at 2.136(4) Å may be considered effectively single,[33] if compared to those found in, for example, $TeMe_4$ [equatorial: 2.127(6); axial: 2.275(17), 2.309(13) Å][34] and $TePh_4$ [equatorial: 2.12(1)−2.16(1) Å; axial 2.26(1)−2.31(1) Å].[35] The W−C(1) and Fe−C(1) bond lengths of 2.127(5) and 1.937(5) Å may be compared with Mo−C(1) and Fe−C(1) in **5d-S**, which are 2.153(2) and 1.942(2) Å, respectively. Thus the W−C(1)−Fe core of **5a-Te** differs slightly from that of **5d-S**, bringing C(1) closer to W, and Fe further from both C(1) and W. Precedent for W−Te bonding includes the complexes [$W({=}Te)_2(PMe_3)_4$] [2.596(1) Å],[36] [$WH_2(\eta^2\text{-}Te_2)(PMe_3)_4$] [2.856(2), 2.903(2) Å] and [$W(\eta^2\text{-}Te_2)(PMe_3)(CNCMe_3)_4$] [2.868(2), 2.877(2) Å],[37] [$W(TePh_2)(CO)_5$] [2.809(1) Å],[38] and [$\{W(CO)_2(\eta\text{-}C_5H_4CO_2Et)\}_2(\mu\text{-}TePh)_2$] [av 2.816(1) Å],[39] which might be considered as benchmarks for telluride, ditellurido, telluroether, and μ-tellurolate coordination. Thus the W−Te bond length of 2.7687(5) Å in **5a-Te** appears somewhat short; however, in the context of cluster chemistry, comparison with the complex [$WFe_2(\mu\text{-}Te)_2(CO)_{10}$] [W−Te 2.736(1) Å][40] (and less precisely [$W_{1.2}Mo_{0.8}Fe(\mu_3\text{-}Te)_2(CO)_7$] [M−Te 2.790 Å][41]) suggests nothing untoward. Indeed, this may be merely a reflection of electron delocalization within clusters. Despite occupying an exposed position on the surface of the molecule, the Te is not involved in any particularly short intermolecular contacts; the shortest contact is 3.19 Å to H−C(10).

Molecular Structure of [$WFe(\mu\text{-}TeCR^1)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)$] (6-Te). The molecular structure of **6-Te** is depicted in Figure 2. Initial inspection indicates that introduction of the dppm bridging ligand does not substantially perturb the WFeCTe core, which retains an orthogonal (88°) relationship between the W−Fe and C(1)−Te bonds. There is also a similar short approach [2.795(10) Å] of the carbonyl carbon C(14) to the iron center. Table 2 compares geometrical parameters for this tetrahedrane with those for **5a-Te** and **5d-S**. The most noticeable difference is that the inclusion of the dppm bridge slightly shortens the W−Fe bond (2.7741(15) Å cf. 2.7884(7) Å in **5a-Te**). This shortening is presumably due to the constraints of chelation rather than any buildup of electron density within the tetrahedrane, which would be expected to expand the framework. Indeed, with the exception of this bond length and that for Fe−Te, which is marginally increased, all other bond lengths within the tetrahedrane are essentially invariant. It is perhaps noteworthy that the bulky dppm ligand bridges adjacent to the tellurium, rather than the more sterically modest alkylidyne group.

Molecular Structure of [$WFe_2(\mu\text{-}CR^2)(\mu_3\text{-}Te)(CO)_7(\eta\text{-}C_5H_5)$] (7a). The molecular structure of the cluster **7a-Te** is shown in Figure 3. The crystal structure of the cluster [$WFe_2(\mu\text{-}CR^1)(\mu_3\text{-}S)(CO)_7(\eta\text{-}C_5H_5)$] (**7f-S**)[27] provides a point of reference for interpreting data for **7a-Te**, and accordingly Table 3 reproduces key geometric parameters for both these compounds. While these two studies should provide an ideal stage for comparing the effects of tellurium and sulfur on cluster geometries, the caveat must be noted that the 2-xylylmethylidyne ligand is sterically cumbersome compared to the 4-toluidyne, and steric factors have been seen to control the chemistry of the former.[24,29] The gross geometries of **7a-Te** and **7f-S** are topologically very similar despite replacement of sulfur with the larger tellurium and of the toluidyne in **7f-S** with the sterically cumbersome $C_6H_3Me_2$-2,6 group. The most significant change involves a lengthening of the Fe(1)−Fe(2) bond length in **7a-Te** (2.683(2) Å) relative to that in **7f-S** (2.645(3) Å), the W−Fe(1) and W−Fe(2) bond lengths remaining essentially unchanged. Similarly, the W−C(1) and Fe(1)−C(1) bond lengths appear to be insensitive (within the greater statistical uncertainties associated with

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(30) A CCDC[31] search based on a three-membered TR−C−Te ring connectivity (any bonding) harvested only the tellurophene salt [$Ru(\eta^5\text{-}TeC_4H_4)(\eta\text{-}C_5Me_5)$]OTf,[32] the mononuclear telluroformaldehyde complex [$TaH(\eta^2\text{-}TeCH_2)(\eta\text{-}C_5Me_5)_2$],[7b] and the diiron complexes [$Fe_2(\mu\text{-}TeCH_2)_2(CO)_6$][10e] and [$Fe_2(\mu\text{-}TeCHMe)(\mu\text{-}SCHMe)(CO)_6$].[10f]

(31) Cambridge Crystallographic Data Centre, CSD version 5-24, November 2002.

(32) Ryu, E.-H.; Chang, H.-Y.; Choi, M.-G. *Bull Korean Chem. Soc.* **1998**, *19*, 706.

(33) Rare examples of structurally characterized molecules featuring formally double C=Te bonds include $O(C_2H_4)_2N{-}CH{=}Te$ [2.043(9) Å] and $MeNC_3H_6C{=}Te$ [2.05(2) Å],[15c] [$C_6H_4(CMe_2)_2C{=}Te{-}W(CO)_5$] [1.987(5) Å],[13d] and the telluroureas $R_2C_2(NMes)_2C{=}Te$ [R = Cl 2.050(3) Å; R = H, 2.066(3) Å].[15d] From these limited data it is clear that the presence of π-conjugative amino substituents reduces the degree of C=Te multiple bonding.

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(38) Liaw, W.-F.; Chiang, M.-H.; Lai, C.-H.; Chiou, S.-J.; Lee, G.-H.; Peng, S.-M, *Inorg. Chem.* **1994**, *33*, 2493.

(39) Song, L.-C.; Shi, Y.-C.; Hu, Q.-M.; Chen, Y.; Sun, J. *J. Organomet. Chem.* **2001**, *626*, 192.

(40) Mathur, P.; Chakrabarty, D.; Hossain, M. M.; Rashid, R. S.; Rugmini, V.; Rheingold, A. L. *Inorg. Chem.* **1992**, *31*, 1106.

(41) Zheng, B.; Huang, J.; Zhang, Q.; Lu, J. *Acta Crystallogr.* **1991**, *C47*, 1090.

Table 3. Comparison of Geometric Parameters (Å, deg) for the Complexes $[WFe_2(\mu_3\text{-}A)(\mu\text{-}Cr)(\mu\text{-}CO)(CO)_6(\eta\text{-}C_5H_5)]$

	A, R	
	Te, R^2 (**7a-Te**)	S, R^1 (**7f-S**)[a,27]
W−Fe(1)	2.770(2)	2.742(3)
W−Fe(2)	2.781(2)	2.777(2)
Fe(1)−Fe(2)	2.683(2)	2.645(3)
W−A	2.6777(9)	2.322(4)
Fe(1)−A	2.563(2)	2.264(7)
Fe(2)−A	2.521(2)	2.205(5)
W−C(1)	1.888(11)	1.87(3)
Fe(1)−C(1)	2.204(12)	2.12(1)
Fe(2)−C(15)	2.660(15)	2.51(2)
W−C(1)−C(2)	150.8(9)	146.6(12)
Fe(1)−C(1)-C(2)	124.2(8)	126.7(14)
W−C(1)−Fe(1)	84.8(5)	86.7(8)

[a] Numbering used in ref 27 replaced for consistency with that used for **7a**.

metal−carbon bond lengths) to the replacement of the chalcogen and alkylidyne substituents, although there is a slight lengthening of the Fe(1)−C(1) bond in **7a-Te** compared with that in **7f-S**. The steric bulk of the alkylidyne is however reflected in a ca. 4° increase in the W−C(1)−C(2) angle to 150.8(9)°. The short W−C(1) separation of 1.888(11) Å is almost comparable to that found in terminal alkylidyne complexes with the same substituent, e.g., $[W(\equiv CR^2)(CO)_2L(\{H_2B(pz)_2\}]$ (L = picoline 1.810(6) Å, PMe_2Ph 1.825(4) Å)[42] and clearly shorter than those found in the W−W edge-bridging alkylidyne ligand in $[W_2Re(\mu\text{-}CR^1)(\mu_3\text{-}CR^1)(\mu\text{-}Br)(\mu\text{-}L)\text{-}(CO)_3(\eta\text{-}C_5H_5)_2]$ (L = CO: 1.954(12), 1.993(12) Å, O: 1.933(19). 2.071(18) Å).[19] The short W−C bond length and opening of the W−C(1)−C(2) angle in **7f-S** have been discussed in terms of semibridging character for the alkylidyne[27] (cf. semibridging carbonyls), and a similar description seems appropriate for **7a-Te**. A further point of note in comparing the structures of **7a-Te** and **7f-S** is that while the tungsten-bound carbonyl in **7f-S** shows appreciable semibridging character [2.51(2) Å], in the case of **7a-Te** this separation is increased to 2.660(15) Å such that its coordination to tungsten is essentially terminal in nature.

Concluding Remarks. While the above results demonstrate parallels between the reaction and structural chemistry of bimetallic complexes of telluroacyl ligands and analogues based on the lighter chalcogens, differences have also emerged. Each of these may be traced to the comparative weakness of C−chalcogen bonds on descending group 16. Nevertheless, telluroacyls have now been shown to serve as ligands in bimetallic compounds, with two examples having been structurally authenticated. The facile inferred conversion of one such example to a trinuclear cluster with μ-alkylidyne and μ-telluride ligands has also been demonstrated, in the isolation of **7a-Te** from the reaction of **3b** with tellurium.

Experimental Section

Conventional Schlenk and vacuum line techniques were employed for the exclusion of air. Solvents were distilled under nitrogen from appropriate drying agents. The alkylidyne complexes $[W(\equiv CR^1)(CO)_2(\eta\text{-}C_5H_5)]$ (**1a**),[43] $[W(\equiv CR^2)(CO)_2(\eta\text{-}C_5H_5)]$ (**1b**),[24] and $[MFe(\mu\text{-}CR^2)(CO)_5(\eta\text{-}C_5H_5)]$ (M = W (**3b**), Mo (**3c**))[24] are described elsewhere. Light petroleum refers to that fraction of boiling point 40−60 °C. Chromatographic separations were routinely performed using a cryostatically cooled column at −30 °C. ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM EX270 NMR spectrometer and referenced against internal Me_4Si (^1H), internal $CDCl_3$ (^{13}C), or external H_3PO_4 (^{31}P). Infrared spectra were recorded using Perkin-Elmer 1720-X FT-IR or Mattson Series 1 spectrometers. FAB mass spectra were measured with an Autospec Q mass spectrometer using 3-nitrobenzyl alcohol as matrix. Elemental microanalytical data were obtained commercially from the University of North London Analytical Service.

Syntheses of $[WFe(\mu\text{-}CR^1)(CO)_n(\eta\text{-}C_5H_5)]$ (n = 5 (3a), 6 (2a)). A mixture of $[W(\equiv CR^1)(CO)_2(\eta\text{-}C_5H_5)]$ (**1a**: 0.75 g, 1.84 mmol) and $[Fe_2(CO)_9]$ (1.34 g, 3.70 mmol) was stirred together in diethyl ether (15 mL) for 16 h in vacuo, with the flask being reevacuated every 5 min for the first hour. The resulting solution was evaporated to dryness, then extracted with a 2:1 light petroleum/dichloromethane mixture. The combined extracts were chromatographed (silica gel, −30 °C), eluting with the same solvent mixture. The first, purple, band was collected and identified as $[WFe(\mu\text{-}CR^1)(CO)_5(\eta\text{-}C_5H_5)]$ (**3a**). Yield: 50 mg (5%). Continued elution gave a broad brown band, which was collected and identified as $[WFe(\mu\text{-}CR^1)(CO)_6(\eta\text{-}C_5H_5)]$ (**2a**) (by comparison with previously reported data[23,44] and those for $[WFe(\mu\text{-}CR^1)(CO)_n(\eta\text{-}C_5Me_5)]$[25]). Yield: 0.41 g (38%).

Synthesis of $[WFe(\mu\text{-}TeCR^1)(CO)_5(\eta\text{-}C_5H_5)]$ (5a-Te). A mixture of $[WFe(\mu\text{-}CR^1)(CO)_6(\eta\text{-}C_5H_5)]$ (**2a**, 0.38 g, 0.66 mmol) and tellurium powder (0.30 g, 2.35 g atom, excess) in tetrahydrofuran (20 mL) was stirred for 1 h, after which time the reaction was found to be complete by infrared spectroscopy. The solvent was removed in vacuo and the residue extracted with a 2:1 light petroleum/dichloromethane mixture. The combined extracts were chromatographed (silica gel, −30 °C), eluting with the same solvent mixture to provide, after removal of solvent, a dark red-brown crystalline solid (0.25 g, 56%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of light petroleum into a dichloromethane solution of **5a-Te**. Anal. Found: C, 32.0; H, 1.5. Calcd for $C_{18}H_{12}O_5FeTeW$: C, 32.00; H, 1.79. FAB-MS (+ve ion): m/z 674 $[M - 2H]^+$, 594 $[M - 3CO]^+$, 537 $[M - Fe(CO)_3 + H]^+$. IR light petroleum: ν_{CO} = 2049s, 1990vs, 1978m, 1913w br, 1860vw br cm^{-1}. Tetrahydrofuran: ν_{CO} = 2038vs, 1978vs, 1965s, 1950sh w, 1905w br cm^{-1}. NMR ($CDCl_3$, 25 °C): ^1H 2.29 (s, 3 H, CH_3), 5.29 (s, 5 H, C_5H_5), 6.93, 7.13 (br × 2, $(AB)_2$, 4 H, $^3J_{AB}$ not resolved suggesting onset of fluxionality). $^{13}C\{^1H\}$: 214.4 (μ-CO), 210.6 (FeCO), 210.2 (WCO), 172.7 (CTe), 154.3 $[C^1(C_6H_4)]$, 135.5 $[C^4(C_6H_4)]$, 129.4, 129.0 $[C^{2,3,5,6}(C_6H_4)]$ 89.3 (C_5H_5), 21.1 (CH_3) ppm. *Crystal data*: $C_{18}H_{12}O_5FeTeW$, M = 675.58, triclinic, $P\bar{1}$ (no. 2), a = 7.9735(6) Å, b = 9.1869(9) Å, c = 12.9588(12) Å, α = 102.399(8)°, β = 99.133(7)°, γ = 94.638(8)°, V = 908.83(14) Å^3, Z = 2, D_c = 2.469 g cm^{-3}, μ(Mo Kα) = 8.720 mm^{-1}, T = 203 K, deep red prisms; 3186 independent measured reflections, F^2 refinement, R_1 = 0.026, wR_2 = 0.068, 3019 independent observed absorption-corrected reflections $[|F_o| > 4\sigma(|F_o|), 2\theta_{max} = 50°]$, 236 parameters. CCDC 228397.

Synthesis of $[WFe(\mu\text{-}TeCR^1)(\mu\text{-}dppm)(CO)_3(\eta\text{-}C_5H_5)]$ (6-Te). A mixture of $[WFe(\mu\text{-}TeCR^1)(CO)_5(\eta\text{-}C_5H_5)]$ (**5a-Te**) (75 mg, 0.11 mmol) and dppm (43 mg, 0.11 mmol) was heated at reflux in benzene (10 mL) for 40 h. The solvent was evaporated and the residue extracted with a 1:1 mixture of diethyl ether and light petroleum. Column chromatography (silica gel, −30 °C) eluting with the same solvent mixture gave a red-brown solution, which was evaporated to dryness, affording dark

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brown, air stable microcrystals. Yield: 63 mg (57%). Crystals of the dichloromethane monosolvate suitable for X-ray diffraction analysis were grown by diffusion of light petroleum into a dichloromethane solution. Anal. Found: C, 48.9; H, 3.4. Calcd for $C_{41}H_{34}O_3FeP_2TeW$: C, 49.05; H, 3.41. FAB-MS (+ve ion): *m/z* 1006 $[M + 2H]^+$, 950 $[M - 2CO]^+$, 922 $[M - 3CO]^+$. IR light petroleum: $\nu_{CO} = 1970$m, 1911vs, 1816w cm^{-1}. NMR (CDCl$_3$, 25 °C): δ 2.26 (s, 3 H, CH$_3$), 3.74 (ddd, 1 H, $^2J_{HH} = 13.7$, $^2J_{PAH} \approx {}^2J_{PBH} = 10.5$, P$_2CH_2$) 4.76 (s, 5 H, C$_5H_5$), 4.98 (ddd, 1 H, $^2J_{HH} = 13.7$, $^2J_{PAH} \approx {}^2J_{PBH} = 9.8$, P$_2CH_2$), 6.89 (d, 2 H, AB, $^3J_{AB} = 8$ Hz, C$_6$H$_4$), 7.00−7.70 (m, 22 H, C$_6$H$_4$ and C$_6$H$_5$). ^{13}C{^{1}H}: 234.4 (d, μ-CO, $^2J_{PC} = 9$), 218.4 (d, FeCO, $^2J_{PC} = 5$), 216.0 (d, FeCO, $^2J_{PC} = 5$), 178.5 (dd, μ-*C*Te, $^2J_{PC} = 25$ & 37), 157.5 [s, C^1(C$_6$H$_4$)], 142.0−127.0 (32 peaks, C$_6$H$_4$ and C$_6$H$_5$), 88.1 (C$_5$H$_5$), 43.8 (dd, P$_2$CH$_2$, $^1J_{PC} = 17$, 18 Hz), 21.0 (CH$_3$) ppm. ^{31}P{^{1}H}: 15.9 (d, $^2J_{PP} = 100$, $^1J_{PW} = 272$), 48.5 (d, $^2J_{PP} = 100$ Hz) ppm. *Crystal data*: $C_{41}H_{34}O_3P_2FeTeW\cdot CH_2Cl_2$, $M = 1088.85$, monoclinic, $P2_1/n$ (no. 14), $a = 11.642(3)$ Å, $b = 17.484(6)$ Å, $c = 20.470(3)$ Å, $\beta = 104.196(13)°$, $V = 4039.4(17)$ Å^3, $Z = 4$, $D_c = 1.790$ g cm^{-3}, μ(Mo Kα) = 4.162 mm^{-1}, $T = 293$ K, deep orange-red blocks; 7099 independent measured reflections, F^2 refinement, $R_1 = 0.051$, $wR_2 = 0.103$, 4620 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 396 parameters. CCDC 228398.

Synthesis of [WFe$_2$(μ-CR^2)(μ_3-Te)(CO)$_7$] (7a-Te). A mixture of [WFe(μ-CR^2)(CO)$_5$(η-C$_5$H$_5$)] (**3b**, 0.85 g, 1.50 mmol) and tellurium powder (0.60 g, 4.70 mmol, excess) in tetrahydrofuran (20 mL) was irradiated in an ultrasonic cleaning bath for 8 h. The solvent was removed in vacuo and the residue redissolved in a 2:1 mixture of light petroleum and dichloromethane and chromatographed (silica gel, −40 °C), eluting with the same solvent mixture. The dark brown band which eluted first was reduced in volume, and the product precipitated by addition of further petrol, giving **7a-Te** as a brown, slightly air-sensitive powder. Yield: 0.26 g (42%). Crystals suitable for X-ray diffraction analysis were grown by diffusion of light petroleum into a dichloromethane solution of **7a-Te**. Anal. Found: C, 31.7; H, 1.9. Calcd for $C_{21}H_{14}O_7Fe_2TeW$: C, 31.47; H, 1.76. FAB-MS (+ve ion) *m/z* 690 $[M - Fe(CO)_2]^+$, 662 $[M - Fe(CO)_3]^+$, 562 $[M - Te - Fe(CO)_2]^+$. IR Nujol: $\nu_{CO} = 2042$s, 2003vs, 1963vs, 1958s sh, 1945w sh, 1832vw cm^{-1}. CHCl$_3$: $\nu_{CO} = 2048$s, 2007vs, 1982s, 1951s sh cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H: 1.98, 2.07 (s × 2, 3 H × 2, CH$_3$), 5.59 (s, 5 H, C$_5$H$_5$), 6.97−7.24 (m, 3 H, C$_6$H$_3$). ^{13}C{^{1}H} (−60 °C): 319.1 (μ-CR^2), 237.5 (μ-CO), 213.4, 209.3 (FeCO), 157.8 [C^1(C$_6$H$_3$)], 130.6, 128.4 [C^{2,6}(C$_6$H$_3$)], 128.3, 128.2 [C^{3,5}(C$_6$H$_3$)], 127.2 [C^4(C$_6$H$_3$)], 93.9 (C$_5$H$_5$), 21.9, 20.7 (CH$_3$) ppm. *Crystal data*: $C_{21}H_{14}O_7Fe_2TeW$, $M = 801.47$, monoclinic, $P2_1/n$ (no. 14), $a = 8.953(4)$ Å, $b = 19.320(4)$ Å, $c = 13.108(3)$ Å, $\beta = 91.12(2)°$, $V = 2266.9(12)$ Å^3, $Z = 4$, $D_c = 2.348$ g cm^{-3}, μ(Mo Kα) = 7.626 mm^{-1}, $T = 293$ K, deep orange-red platy needles; 3728 independent measured reflections, F^2 refinement, $R_1 = 0.052$, $wR_2 = 0.125$, 2933 independent observed absorption corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 50°$], 292 parameters. CCDC 228399.

Synthesis of [MoFe(μ-TeCR^2)(CO)$_5$(η-C$_5$H$_5$)] (5b-Te) and [MoFe$_2$(μ-CR^2)(μ-Te)(CO)$_7$(η-C$_5$H$_5$)] (7b-Te). A mixture of [MoFe(μ-CR^2)(CO)$_5$(η-C$_5$H$_5$)] (**3c**, 0.80 g, 1.70 mmol) and tellurium powder (0.60 g, 4.70 g atom, excess) in tetrahydrofuran (20 mL) was irradiated in an ultrasonic cleaning bath for 1 h. The solvent was removed in vacuo and the residue extracted with a 2:1 mixture of light petroleum and dichloromethane and chromatographed (silica gel, −40 °C), eluting with the same solvent mixture. The dark brown band which was eluted first was reduced in volume to dryness to provide a 1:0.8 mixture (^{1}H NMR integration) of **5b-Te** and **7b-Te**. Further purification by flash chromatography on silica gel using light petroleum ether as eluent provided a pure sample of **5b-Te** as an air stable, dark brown microcrystalline solid (25 mg, 2.5%). Anal. Found: C, 37.8; H, 2.3. Calcd for $C_{19}H_{14}O_5FeMoTe$: C, 37.93; H, 2.35. FAB-MS (+ve ion) *m/z* 602 $[M + 2H]^+$, 460 $[M - 5CO - 4H]^+$. IR light petroleum: $\nu_{CO} = 2048$s, 2007vs, 1980s br, 1951w br cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H: δ 2.46 (s br, 6 H, CH$_3$), 5.09 (s, 5 H, C$_5$H$_5$), 6.93−7.06 (m, 3 H, C$_6$H$_3$). ^{13}C{^{1}H}: 229.9, 227.5 (MoCO), 210.5, 210.0 (FeCO), 163.0 (CTe), 156.6 [C^1(C$_6$H$_3$)], 128.6−125.4 (C$_6$H$_3$), 92.7 (C$_5$H$_5$), 27.7, 20.8 (br, CH$_3$) ppm. Spectroscopic data for **7b-Te** were obtained from the mixture of **7b-Te** and **5b-Te** described above. IR (light petroleum, ν_{CO}): 2036s, 2010vs, 1999m, 1965m, 1901w, 1868vw cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H: δ 2.04, 2.15 (s br × 2, 6 H, CH$_3$), 5.55 (s, 5 H, C$_5$H$_5$), 6.92−7.07 (m, 3 H, C$_6$H$_3$). ^{13}C{^{1}H}: 347.1(μ-CR^2), 245.9 (MoCO), 213.8 (br, FeCO), 154.3 [C^1(C$_6$H$_3$)], 128.6−125.4 (C$_6$H$_3$), 95.8 (C$_5$H$_5$), 21.9, 20.8 (CH$_3$) ppm.

Synthesis of [WFe$_2$(μ-CR^2)(μ_3-Te)(μ-dppm)(CO)$_5$(η-C$_5$H$_5$)] (8b-Te). A mixture of [WFe$_2$(μ-CR^2)(μ_3-Te)(CO)$_7$(η-C$_5$H$_5$)] (**7a-Te**) (50 mg, 0.073 mmol) and dppm (50 mg, 0.13 mmol, excess) were heated at reflux in benzene (10 mL) for 16 h. The solvent was evaporated and the residue dissolved in a 1:1 mixture of diethyl ether and light petroleum. Column chromatography (silica gel, −30 °C) eluting with the same solvent mixture gave an initial orange band of [W($\equiv$CR^2)(CO)$_2$(η-C$_5$H$_5$)] (**1b**), followed by a dark brown band, which was collected and evaporated to dryness, affording a dark brown, air stable powder. Yield: 15 mg (18%). Anal. Found: C, 47.5; H, 3.1. Calcd for $C_{44}H_{36}O_5P_2Fe_2TeW$: C, 46.77; H, 3.21. FAB-MS (+ve ion) *m/z* 1129 $[M - H]^+$, 1075 $[M - 2CO + H]^+$, 1018 $[M - Fe(CO)_2]^+$, 990 $[M - Fe(CO)_3]^+$, 507 $[M + H - Te - dppm - Fe(CO)_2]^+$. IR Nujol: $\nu_{CO} = 1976$m, 1936s, 1911m, 1903w br cm^{-1}. Light petroleum: $\nu_{CO} = 1978$m, 1938vs, 1891m br cm^{-1}. NMR (CDCl$_3$, 25 °C): ^{1}H: δ 1.94, 2.11 (s × 2, 3 H × 2, CH$_3$), 3.41 (ddd, 1 H, $^2J_{HH} = 16.4$, $^2J_{PAH} \approx {}^2J_{PBH} = 9.6$, P$_2CH_2$), 4.50 (ddd, 1 H, $^2J_{HH} = 16.4$, $^2J_{PAH} \approx {}^2J_{PBH} = 11.0$, P$_2CH_2$), 5.45 (s, 5 H, C$_5H_5$), 6.80−7.90 (m, 23 H, C$_6H_5$ and C$_6$H$_3$). ^{13}C{^{1}H}: 313.2 (μ-CR^2), 222.4 (d, μ-CO, $^2J_{PC} = 21$), 216.3, (d, FeCO, $^2J_{PC} = 18$), 214.4 (d, FeCO, $^2J_{PC} = 25$ Hz), 158.9 [C^1(C$_6$H$_3$)], 145.0−122.0 (C$_6$H$_3$ and C$_6$H$_5$), 93.8 (C$_5$H$_5$), 38.0 (P$_2$CH$_2$), 21.8, 21.4 (CH$_3$ × 2) ppm. ^{31}P{^{1}H}: 59.5 (d, $^{2,3}J_{PP} = 76$, $^2J_{PW} = 98$), 63.7 (d, $^{2,3}J_{PP} = 76$, $^2J_{PW} = 45$ Hz).

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Supporting Information Available: Full details of the crystal structure determinations of compounds **5a-Te**, **6-Te**, and **7a-Te**. This material is available free of charge via the Internet at http://pubs.acs.org.

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