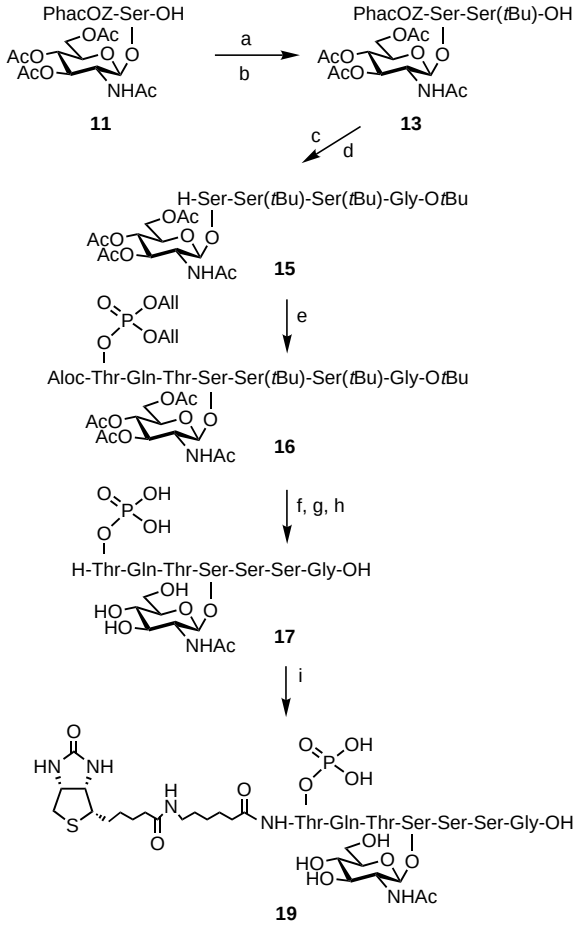

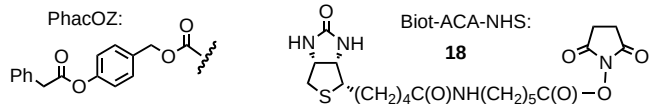

Scheme 3. Synthesis of a biotinylated glycophosphopeptide from the transactivation domain of the serum response factor. a) H-Ser(*t*Bu)-OCho (**12**), DIC, HOBt, CH_2Cl_2, 73%; b) butyrylcholine esterase, 0.01M phosphate buffer, pH 6.5, 37°C, 88%; c) H-Ser(*t*Bu)-Gly-O*t*Bu (**14**), DIC, HOBt, CH_2Cl_2, 78%; d) penicillin G acylase, 0.7M phosphate buffer/methanol (70/30, pH 7), NaI (500 equiv), room temperature (RT), 65%; e) Aloc-Thr(P(O)(OAll)$_2$)-Gln-Thr-OH (**7**), DIC, HOBt, CH_2Cl_2, 74%; f) $(PPh_3)_4Pd$, HCOOH/*n*BuNH$_2$ (10 equiv/6 equiv), RT; g) F_3CCOOH; h) hydrazine hydrate (3000 equiv), methanol, RT, 40% (three steps); i) Biot-ACA-NHS (**18**), DMF, 68%.

In conclusion we have devised a new and efficient strategy for the synthesis of glycosylated and phosphorylated peptides based on the combination of suitable enzyme-labile protecting groups. By means of this methodology acid- and base-sensitive biologically relevant labeled peptide conjugates can be built up, which may open up new avenues of research in biology and bioorganic chemistry. In particular, they should serve to unravel the chemical biology of the serum respone factor and the importance of its posttranslational modification in molecular detail.

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$[(TeMe_2)Mn(CO)_4(\mu_5\text{-}Te)(\mu_4\text{-}Te)Mn_4(CO)_{12}]^-$: A Pentacoordinate Bridging Tellurido Ligand in a Square-Pyramidal Geometry**

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Chalcogen-containing transition metal carbonyl complexes have attracted much attention recently due to their versatile bonding modes and reactivity.[1] Nevertheless, Mn – Te – CO clusters have remained unknown despite considerable advances in the corresponding chemistry of Fe – Te – CO clusters.[2, 3] We have discovered a simple and efficient route to this new family of clusters that involves the direct thermal reaction of the common reagents $[Mn_2(CO)_{10}]$ and K_2TeO_3. In contrast to the well-studied Fe system, the new Mn – Te clusters are based on octahedra with μ_4-Te centers.

The parent cluster **1** (PPN = $[P(C_6H_5)_3]_2N^+$) was synthesized by the reaction of K_2TeO_3 with $[Mn_2(CO)_{10}]$ in methanol

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followed by precipitation with [PPN]Cl. The Te-metalated complex **2** was obtained from **1** and $MeSO_3CF_3$ in CH_2Cl_2. The cluster anions of **1** and **2** represent the first examples of tellurido manganese carbonyl clusters; each contains four manganese–manganese bonds.

$[PPN]_2[(\mu_4\text{-Te})_2Mn_4(CO)_{12}]$ **1**

$[PPN][(TeMe_2)Mn(CO)_4(\mu_5\text{-Te})(\mu_4\text{-Te})Mn_4(CO)_{12}]$ **2**

A variety of coordination modes are observed for tellurido ligands in transition metal complexes.[4, 5] Doubly and triply bridging tellurido ligands are common, but quadruply bridging tellurido ligands are much rarer[1, 2, 4, 5] due to the decreased basicity of the tellurium atom compared to its congeners. The only two previous examples of complexes with the bridging μ_5-Te ligands in a pyramidal mode are $[Ni_9Te_6(PEt_3)_8]$ and $[Ni_{20}Te_{18}(PEt_3)_{12}]$.[6] Here we describe for the first time the ability of the Te^{2-} ligand in the pyramidal $TeMn_4$ unit to bind another metal center in an axial fashion.

X-ray structure analysis shows that the anion of **1** has an octahedral geometry with two μ_4-Te ligands and four seven-coordinate manganese atoms (Figure 1).[7] Structurally characterized complexes containing μ_4-Te ligands include $[(\mu_4\text{-Te})_2Ru_4(CO)_{11}]$,[8] $[(\mu_4\text{-Te})_2Ru_2Fe_2(CO)_{11}]$,[9] $[(\mu_4\text{-Te})(\mu_3\text{-Te})Fe_2Os_3(CO)_{17}]$,[10] $[\{Fe_2(CO)_6\}(\mu_4\text{-Te})(\mu_3\text{-Te})\{Ru_3(CO)_{11}\}]$,[11] $[(\mu_4\text{-Te})_2Co_4(CO)_6(Et_3P)_4]$,[12] $[Co_{11}Te_7(CO)_{10}]^{2-}$,[13] $[Ru_6(Te_2)_7(CO)_{12}]^{2-}$,[14] and $[(\mu_4\text{-Te})_2Fe_4(CO)_{11}]$.[15] However, the lone pair of the μ_4-Te atom was not shown to be chemically active, and its basicity has not been demonstrated in transition metal complexes.

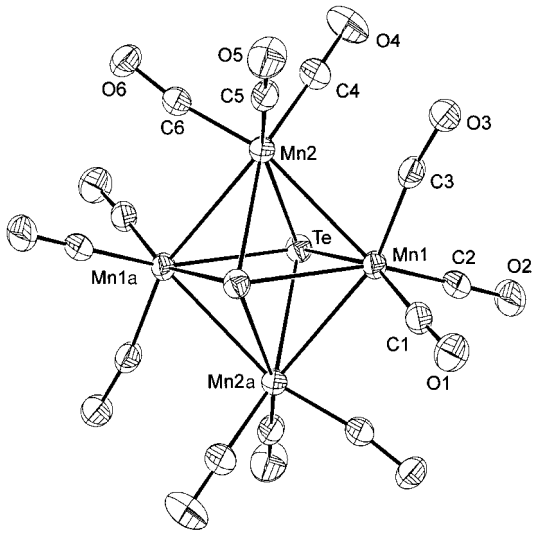

Figure 1. Crystal structure of the dianion of **1** (30% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Te–Mn1 2.6363(8), Te–Mn1a 2.6355(6), Te–Mn2 2.6482(8), Te–Mn2a 2.6444(7), Mn1–Mn2 2.7976(8), Mn1–Mn2a 2.8237(9); Mn1-Te-Mn1a 97.42(2), Mn2-Mn1-Mn2a 90.40(2), Mn1-Mn2-Mn1a 89.60(2).

The question arises whether the basicity of Te is affected by the transition metal centers. Increased basicity of Te might be expected owing to the more electropositive character of Mn. We therefore attempted the alkylation of **1**. Careful methylation of **1** with $MeSO_3CF_3$ led to the isolation of the unexpected Te-metalated complex **2**, in which a quadruply bridging tellurido ligand is externally bonded to a $Mn(CO)_4$-$TeMe_2$ fragment, presumably by formation of a Te→Mn donor–acceptor bond. The structure of **2** was determined by single-crystal X-ray analysis (Figure 2).[7] The ^1H NMR spectrum of the anion of **2** showed signals at $\delta = 2.18$ and 2.14, similar to that of the methyltellurido ligands in $[Fe_4(Te_2)_2(Te)_2(TeMe)_2(CO)_8]^{2-}$ ($\delta = 2.2$).[16]

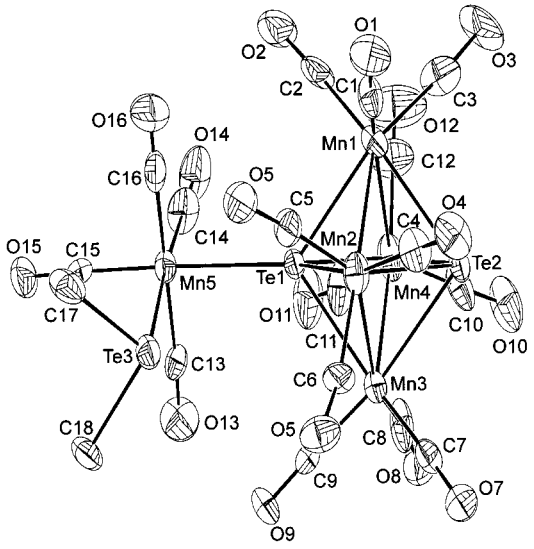

Figure 2. Crystal structure of the anion of **2** (30% thermal ellipsoids). Selected bond lengths [Å] and angles [°]: Te1–Mn1 2.601(3), Te1–Mn2 2.577(3), Te1–Mn3 2.602(3), Te1–Mn4 2.577(3), Te1–Mn5 2.643(3), Te2–Mn1 2.632(3), Te2–Mn2 2.647(3), Te2–Mn3 2.638(3), Te2–Mn4 2.642(4), Te3–Mn5 2.614 (3), Te3–C av 2.15(2), Mn1–Mn2 2.858(4), Mn1–Mn4 2.837(5), Mn2–Mn3 2.810(5), Mn3–Mn4 2.854(5); Mn2-Mn1-Mn4 89.4(1), Mn1-Mn2-Mn3 90.5(1), Mn2-Mn3-Mn4 90.0(1), Mn1-Mn4-Mn3 90.1(1).

A detailed study showed that the mononuclear cationic species $[Mn(CO)_4(TeMe_2)]^+$ was produced in the course of this reaction, which was monitored by IR spectroscopy.[17] Hence, it is reasonable to assume that the anion of **2** results from the interaction of the dianion of **1** through the μ_4-Te atom with the moiety $[(TeMe_2)Mn(CO)_4]^+$, which could be derived from the fragmentation of cluster **1** upon methylation. However, the role of $MeSO_3CF_3$ is crucial because the attempted reaction of **1** with $[Mn(CO)_5]Br$ failed to give the expected metalated product.

There are several interesting features in **2**. First, the geometry of the μ_5-Te ligand is close to square pyramidal, but slight differences in the Te1–Mn distances and the Mn5-Te1-Mn angles cause a deviation from perfect C_{4v} symmetry. The crystal packing of **2** shows no significant interaction between the cation and the anion or between the anions. The bulky $Te_2Mn_4(CO)_{12}$ group and the $TeMe_2$ moiety are *cis* rather than *trans* to each other. This is explained in terms of the *trans* influence of the $Te_2Mn_4(CO)_{12}$ moiety. Since $Te_2Mn_4(CO)_{12}$ is a not a strong σ-bonding ligand, a strongly σ bonding CO ligand is preferred to a $TeMe_2$ group in the position *trans* to the $Te_2Mn_4(CO)_{12}$ ligand. The (μ_4-Te)–Mn

bond lengths of **2** and **1** are almost equal (2.632 – 2.648 Å). The (μ_5-Te)–Mn bonds of **2** were expected to be significantly longer, but the opposite effect is observed: these bonds are unusually short (2.577 – 2.602 Å).

We have discovered a new family of Te – Mn – CO clusters and a novel μ_5-Te^{2-} bonding mode. Our results strongly suggest the existence of μ_5-Te^{2-} ligands in other early transition metal clusters, and the investigation of this possibility is currently underway.

Experimental Section

All experiments were performed under a nitrogen atmosphere.

1: To a mixture of $[Mn_2(CO)_{10}]$ (0.725 g, 1.86 mmol) and $K_2TeO_3 \cdot H_2O$ (0.236 g, 0.930 mmol) was added MeOH (40 mL). The solution was heated to reflux (110 °C) for 98 h to give a red-brown solution, which was filtered and concentrated. Dropwise addition of a solution of [PPN]Cl (0.705 g, 1.23 mmol) in MeOH precipitated a solid, which was washed several times with deionized water. The residue was recrystallized from CH_2Cl_2/MeOH several times to give 0.44 g (0.233 mmol) of **1** (50 % yield based on Te). IR (CH_2Cl_2): $\tilde{\nu}_{CO} = 1941$ (s), 1884 cm^{-1} (m); elemental analysis calcd for $C_{84}H_{60}Mn_4N_2O_{12}P_4Te_2$: C 53.43, H 3.20, N, 1.48; found: C 53.44, H 3.15, N 1.47. Compound **1** is soluble in CH_2Cl_2, THF, and MeCN, but insoluble in hexanes, Et_2O, and MeOH. Crystals suitable for X-ray analysis were grown from a solution in MeCN.

2: $MeSO_3CF_3$ (0.283 mL, 2.20 mmol) was added to **1** (0.520 g, 0.275 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The solution was allowed to warm to room temperature and stirred for 26 h. The resulting solution was filtered, the solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 and then recrystallized from CH_2Cl_2/hexane several times to give 0.210 g (0.130 mmol) of **2** (78 % yield based on Te). IR (THF): $\tilde{\nu}_{CO} = 2078$ (w), 2008 (m), 1960 (s), 1905 cm^{-1} (m); elemental analysis calcd for $C_{54}H_{36}Mn_5NO_{16}P_2Te_3$: C 38.74, H 2.17, N 0.84; found: C 38.72, H 2.09, N 0.94; ^{1}H NMR (400 MHz, $CDCl_3$, 295 K): $\delta = 2.18$, 2.14. Compound **2** is soluble in Et_2O, CH_2Cl_2, THF, MeCN, and MeOH, but insoluble in hexane. Crystals suitable for X-ray analysis were grown from a solution in Et_2O/CH_2Cl_2.

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[7] a) Crystal data for **1**: $C_{84}H_{60}Mn_4N_2O_{12}P_4Te_2$, $M_r = 1888.24$, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 12.200(2)$, $b = 13.158(3)$, $c = 13.791(2)$ Å, $\alpha = 66.96(2)$, $\beta = 89.63(2)$, $\gamma = 77.46(2)°$, $V = 1981.0(6)$ Å^3, $\rho_{calcd} = 1.583$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.70930$ Å, $\mu = 1.46$ mm^{-1}. A total of 6973 unique reflections were collected on a Nonius CAD-4 diffractometer at 298 K in the range $2.0 < 2\theta < 50°$ with $\theta/2\theta$ scans, and an absorption correction by azimuthal ψ scans was applied. The structure was solved by direct methods and refined (NRCC-SDP-VAX packages) by full-matrix least-squares methods to $R = 0.025$ and $Rw = 0.022$ for 5885 observed reflections ($I > 2.5\sigma(I)$) and GOF = 2.27. b) Crystal data for **2**: $C_{54}H_{36}Mn_5NO_{16}P_2Te_3$, $M_r = 1674.30$, triclinic, space group $P\bar{1}$, $Z = 2$, $a = 11.491(4)$, $b = 16.581(5)$, $c = 18.032(4)$, $\alpha = 112.20(3)$, $\beta = 105.19(3)$, $\gamma = 92.86(3)°$, $V = 3027.0(2)$ Å^3, $\rho_{calcd} = 1.837$ g cm^{-3}, $Mo_{K\alpha}$ radiation, $\lambda = 0.70930$ Å, $\mu = 2.51$ mm^{-1}. A total of 10625 unique reflections were collected on a Nonius CAD-4 diffractometer at 298 K in the range $2.0 < 2\theta < 50°$ by using $\theta/2\theta$ scans, and an absorption correction by azimuthal ψ scans was applied. The structure was solved by direct methods and refined (NRCC-SDP-VAX packages) by full-matrix least-squares to $R = 0.053$ and $Rw = 0.046$ for 4109 observed reflections ($I > 6\sigma(I)$) and GOF = 2.84. c) Further details of the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository numbers CSD-408 889 (**1**) and -408 890 (**2**).

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