Multiple Bonds between Transition Metals and 'Bare' Main Group Elements. A Reactive Manganese–Tellurium–Manganese Framework: Synthesis, Structure, and Alkylidene Addition†

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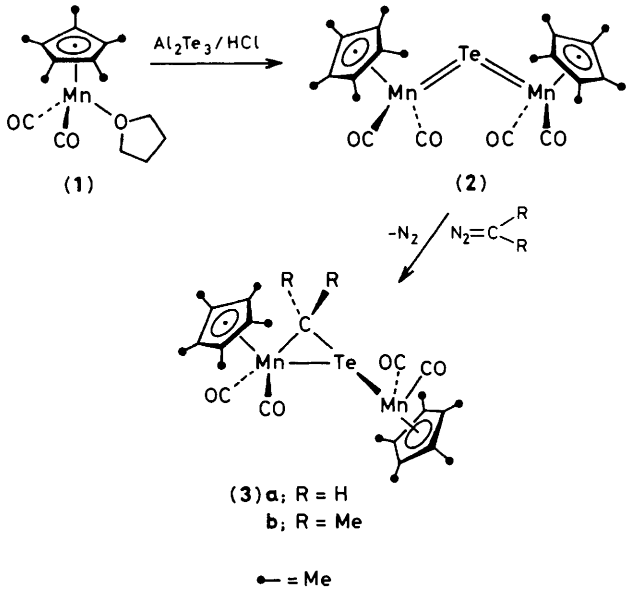
A bent manganese–tellurium–manganese framework exhibiting multiple bond character has been constructed by treatment of the solvent-stabilized organomanganese complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$thf (**1**; thf = tetrahydrofuran) with aluminium telluride in the presence of aqueous hydrochloric acid; the dinuclear product $(\mu\text{-Te})[(\eta^5\text{-}C_5Me_5)Mn(CO)_2]_2$ (**2**) isolated in 46% yield has been shown by *X*-ray crystallography to contain a central 'bare' tellurium bridging atom which is attached to two independent $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$ moieties *via* very short Te–Mn bonds [245.9(2) pm]; this compound reacts readily with diazoalkanes to give μ-alkylidene complexes of composition $(\mu,\eta^2\text{-TeCR}_2)[(\eta^5\text{-}C_5Me_5)Mn(CO)_2]_2$ [(**3a**) R = H, (**3b**) R = Me].

The chemistry of transition metal complexes with bridging alkylidene ligands has developed rapidly since general synthetic routes to these compounds became available.[1,2] One major reliable route to the three-membered frameworks of these metallacyclopropanes is transfer of alkylidene groups from readily accessible diazoalkanes to metal–metal double bonds, a methodology reminiscent of the well-known cyclopropanation of olefins in organic chemistry.[1] In principle, this reaction also works with multiple bonds between transition metals and 'bare' main group elements such as germanium and the chalcogens.[2] However, only very few starting compounds are known that contain authentic multiply bonded structures of type (A) (E = main group element) or related polynuclear cores.[3,4] We therefore set out to develop systematically syntheses of such species and examine both their structures and their reactivity patterns. Here we report on the first bent MnTeMn system and show that alkylidene addition is a facile reaction in such a framework.

Treatment of the tetrahydrofuran (thf) complex $(\eta^5\text{-}C_5Me_5)Mn(CO)_2$thf (**1**) [from photolysis of $(\eta^5\text{-}C_5Me_5)Mn(CO)_3$ in thf] with aluminium telluride in the presence of aqueous hydrochloric acid with subsequent low-temperature column chromatography (Florisil, n-hexane–toluene, −30 °C) and recrystallization of the crude product gave black, lustrous, thermally stable crystals (decomp. *ca.* 186 °C) of composition $C_{24}H_{30}Mn_2O_4Te$ (**2**) in 46% yield (Scheme 1).‡



Scheme 1

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† For Part IV of the series, 'Multiple Bonds between Main Group Elements and Transition Metals,' see W. A. Herrmann, J. Rohrmann, and A. Schäfer, *J. Organomet. Chem.*, 1984, **265**, C1.

‡ Selected spectroscopic data: ν_{CO} (cm^{-1}): 1980vs, 1920vs, 1902s, 1880m (KBr); 1980vs, 1922vs (thf); 1990vs, 1935vs, 1918m, 1905vw, 1880vw (n-hexane); ^{1}H n.m.r. (270 MHz; $CDCl_3$, 25 °C): δ 1.77 (s, CH_3).

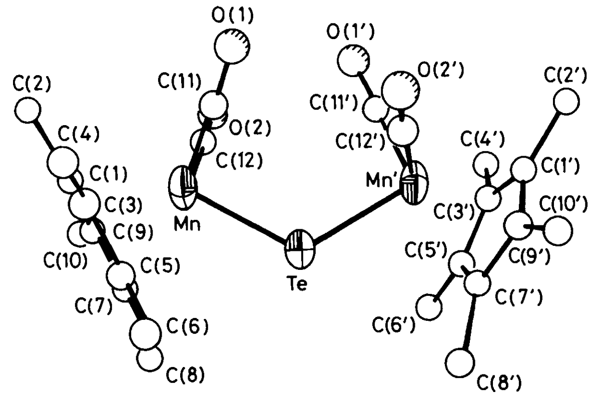

Figure 1. Molecular structure of (μ-tellurio)bis[dicarbonyl(η^5-pentamethylcyclopentadienyl)manganese] (**2**). The thermal ellipsoids are drawn to 50% equiprobability; hydrogen atoms are omitted for clarity. Selected structural parameters: Mn–Te 245.9(2), Mn–C(O) (av.) 176.6(12), C–O (av.) 117.4(15) pm; Mn–Te–Mn' 123.8(1), Mn–C–O (av.) 177.1(11), (O)C–Mn–C(O) 85.7(6)°. Errors are with respect to the least significant digit(s).

The structure of (**2**) shown in Figure 1, was established by a single crystal *X*-ray diffraction study§ and consists of two independent (η^5-C_5Me_5)Mn(CO)$_2$ moieties connected through a 'bare' tellurium atom bridge. Several features are worthy of mention that do not agree with previous observations on related systems: (i) in contrast to the analogous sulphur compound of composition (μ-S)[(η^5-C_5H_5)Re(CO)$_2$]$_2$ (Re–Re 295 pm)[5] there is no metal-to-metal bond present in (**2**); the Mn–Mn distance (420.9 pm) is too long for such a bonding interaction (requiring <324 pm).[6] (ii) The manganese–tellurium contacts are much shorter than those expected for a single-bond interaction. While a distance of *ca.* 270 pm would suggest typical single bond character based on the covalent radii for both atoms (Mn *ca.* 133, Te 137 pm),[7] the observed value of 245.9(2) pm indicates multiple bonding. A similar but less pronounced effect has recently been noted for the related trinuclear complex (μ_3-Te)[(η^5-C_5H_5)Mn(CO)$_2$]$_3$ where the central tellurium atom has almost planar trigonal co-ordination [Mn–Te 248.5 (av.) pm].[8] The $TeMn_3$ core of this last compound may be considered derived from the $TeMn_2$ framework in (**2**) by adding another (C_5H_5)Mn(CO)$_2$ fragment. This process parallels the formation of the chalcogen trioxides XO_3 (planar triangular; *e.g.*, SO_3) from the respective dioxides XO_2 (bent; *e.g.*, SO_2) by the addition of an extra oxygen atom *via* the lone pair at sulphur. The fact that the trinuclear compound (μ_3-Te)[(η^5-C_5Me_5)Mn(CO)$_2$]$_3$ was not observed as a by-product in the formation of (**2**) probably results from steric crowding owing to the bulky C_5Me_5 ligands.

$$L_xM\overset{x}{\text{—}}E\overset{x}{\text{—}}ML_x$$

(A)

x = bond order = no. of ligands L

One interesting reaction of the dinuclear μ-tellurium complex (**2**) is the addition of alkylidene groups as shown in Scheme 1. Thus, diazomethane and 2-diazopropane underwent fast elimination of dinitrogen upon treatment with thf–diethyl ether solutions of (**2**) at *ca.* −30 °C, to give the dark blue, crystalline, air-sensitive complexes (**3a**) and (**3b**), respectively (isolated yields >95%).¶ These compounds may alternatively be regarded as heterodinuclear dimetallacyclopropane-type μ-alkylidene complexes.[1a,9] The CR_2 bridge collapsed when crystalline (**3a**) or (**3b**) was heated at 180 °C, with quantitative carbene–carbene coupling and concomitant formation of ethylene occurring in case of (**3a**). In contrast, facile carbene isomerization to propene (100%) occurred in (**3b**) under thermolysis conditions.

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2 Another useful synthetic strategy has been developed by Knox *et al.*, *cf.* A. F. Dyke, S. R. Finnimore, S. A. R. Knox, P. J. Naish, A. G. Orpen, G. H. Riding, and G. E. Taylor, in 'Reactivity of Metal-Metal Bonds,' ed. M. H. Chisholm, ACS Symposium Series, vol. 155, p. 259, American Chemical Society, Washington, D.C., 1981.

3 Review: W. A. Herrmann, 'Small Hydrocarbons as Bridging Ligands in Transition Metal Chemistry: Synthesis, Structures, and Reactivity,' in 'Organometallic Compounds,' ed. B. L. Shapiro, vol. 1, p. 383 ff., Texas A & M University Press, College Station, Texas, U.S.A., 1983. Bare oxygen and nitrogen atoms exhibiting multiple bonding to transition metals are hitherto largely confined to complexes with the metal atoms in higher oxidation states, *cf.* F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Fourth Edition, Chap. 4, Wiley & Sons, New York 1980.

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§ *Crystal data* for (**2**): $C_{24}H_{30}Mn_2O_4Te$, M = 620.0, rhombic face-centred, space group *F2dd*, a = 8.015(1), b = 15.752(6), c = 41.96(1) Å, $\alpha = \beta = \gamma = 90°$, Z = 8, $F(000)$ = 2464, $3 \leqslant 2\theta \leqslant 50°$ (Syntex AED, Mo-K_α = 0·71069 Å; 2θ scan technique), 836 reflections with $I > 2.5\sigma(I)$, R(iso) = 0.113, R(aniso) = 0.041, R_w = 0.03. The *R*-factors correspond to very little overdetermination of the structure so that bond distances cannot be highly accurate. Atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¶ Selected spectroscopic data: (**3a**), ν_{CO} (cm^{-1}): 1975vs, 1940m, 1920s, 1900vs, 1850vs (KBr); 1980vs, (1945sh), 1928s, 1910vs, 1865s—vs (Et_2O); ^1H n.m.r. (270 MHz; $CDCl_3$, 25 °C): δ 1.76, 1.82 (2 × s, 2 × 15H, CH_3), 5.25 ('s', 1H, CH_2), 5.56 ('s', 1H, CH_2). (**3b**), ν_{CO} (cm^{-1}): 1960vs, 1910s, 1895m, 1845vs, 1820vw (KBr); 1970vs, 1920w, 1900s, 1850 (thf); ^1H n.m.r. (270 MHz; CD_2Cl_2, 25 °C): δ 1.79, 1.83 (2 × s, 2 × 15H, C_5Me_5), 1.87, 1.97 (2 × s, 2 × 3H, CMe_2). Satisfactory C, H, Mn, and Te analyses were obtained for both compounds as well as for the precursor (**2**).