Organometallic Synthesis of Manganese Telluride. Isolation and Characterization of [(Et3P)2(CO)3MnTe]2

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Abstract: As part of a program studying the use of organometallic precursors to prepare solid-state materials, MnTe has been synthesized from (triethylphosphine)telluride (Et3PTe) and dimanganese decacarbonyl ($Mn_2(CO)_{10}$) under mild conditions. An organometallic complex, [(Et3P)2(CO)3MnTe]2 (**1**), has been isolated and characterized. Its crystal and molecular structure has been determined by X-ray diffraction. The structure of **1** is orthorhombic: space group *Pbca*; a = 13.329 (4), b = 13.380 (3), c = 23.644 (8) Å; Z = 4; final R = 0.034 and R_w = 0.047. The dimeric molecule has a structure analogous to a diorganoditelluride, RTeTeR, with (Et3P)2(CO)3Mn– moieties replacing the R groups. It is the first known example of an organometallic molecule having such a ditelluride bridge. Pyrolysis of **1** at 300 °C yields crystalline MnTe. Mechanisms are suggested for the formation of **1** and its transformation to MnTe.

A feature that is quite common to the preparation of inorganic solid-state compounds is high-temperature processing. High temperatures are required because the solid-state precursors must interdiffuse in order to assemble the product structure.[1] While this is not usually a limitation in solid-state synthesis, there are notable cases in which high temperatures must be avoided. For example, sharp interfaces between films of different materials often suffer under drastic preparative conditions, owing to diffusion or evaporation. In a similar way, it often occurs that phases are not stable with respect to structural and/or stoichiometric change above given temperatures. Low-temperature synthesis promises to circumvent these problems.

One general method that is potentially useful as low-temperature synthesis scheme is the use of organometallic starting materials. Since organometallic complexes may be viewed as the constituent elements in molecularly dispersed form, one of the significant barriers to low-temperature synthesis (the interdiffusion of the solid-state precursors) is immediately overcome. In order to use the general technique effectively, one must know, in at least a descriptive way, the chemical routes that lead from organometallic starting materials to inorganic solid-state products. In particular, one must know which organometallic precursors are practical for given product materials. In this work we describe a synthesis of the semiconductor manganese telluride, MnTe, from organometallic starting materials. We also include the interception and characterization of an intermediate organometallic complex, [(CO)3(Et3P)2MnTe]2. Our main conclusions are that this complex is readily formed from independently soluble (i.e., dispersible) reagents and that it pyrolyzes cleanly to MnTe, without detectable formation of other solid-state products such as Mn, Te, or MnTe2.

Owing to the d^5 core of electrons on Mn^{II}, manganese telluride (MnTe) is a so-called magnetic semiconductor. Recent studies of the physics of dilute magnetic semiconductors[2] spurred our interest in possible organometallic routes to this compound. We have recently found[3] that (trialkylphosphine)tellurides are very convenient sources of tellurium in the synthesis of semiconductor materials, acting like a coordination complex of zerovalent tellurium. Therefore, we sought a route to MnTe using the reaction of phosphinetellurides with a complex of zerovalent manganese, $Mn_2(CO)_{10}$.

Experimental Section

Inert-atmosphere drybox and Schlenk-line techniques were used throughout the preparative procedures. Toluene and heptane were anhydrous grade, used as purchased from Aldrich. Dimanganese decacarbonyl was purchased from Aldrich, and tellurium powder (m2n5, –120

Table I. Crystal Data and Details of the Structure Determination of Compound 1

formula	$Mn_2Te_2P_4C_{30}H_{60}$
cryst syst	orthorhombic
space gp[a]	*Pbca*
a, Å	13.329 (4)
b, Å	13.380 (3)
c, Å	23.644 (8)
V, Å^3	4213.2
Z	4
d_{calcd},[b] g/cm^3	1.584
d_{measd},[b] g/cm^3	1.56 (2)
μ(Mo Kα), cm^{-1}	21.1
cryst size, mm	0.2 × 0.2 × 0.2
scan range, deg	3.0 < θ < 25.0
ω scan interval, deg	0.8 + 0.35 tan θ
prescan speed, deg/min	16.48
prescan acceptance $\sigma(I)/I$	1.0
required final $\sigma(I)/I$	0.03
bkgd measd equal to	$^1/_2$ peak time
no. of data colld	3683
no. of obsd data ($I > 3\sigma(I)$)	2527
no. of parameters refined	199
R	0.034
R_w	0.047

[a] The space group assignment was based on axial photographs and systematic absences and confirmed by successful refinement of the structure model. [b] Density measured by flotation in aqueous KI.

mesh), from Alfa; both were used without further purification. (Et3P)2(CO)3MnBr was prepared via literature methods.[4] NMR spectra were recorded on a JEOL FX-90Q spectrometer, UV–visible spectra were recorded on an HP-8451A spectrometer, and IR spectra were recorded on a Perkin-Elmer 683 spectrometer. X-ray diffraction powder patterns were recorded on a Rigaku Miniflex diffractometer.

Synthesis of [(Et3P)2(CO)3MnTe]2. (Triethylphosphine)telluride was prepared by treating Te powder (1.51 g, 11.8 mM) suspended in toluene (20 mL) with Et3P (3.2 g, 27.1 mmol). The mixture was stirred until all of the metal dissolved (gentle heating ($T \le 50$ °C) hastens this process but is not necessary). In a second vessel $Mn_2(CO)_{10}$ (2.30 g, 5.90 mmol) was dissolved in toluene (30 mL), and the solution was treated with Et3P (3.2 g, 27.1 mmol). Via cannula the pale yellow solution of Et3PTe was added all at once at room temperature to the $Mn_2(CO)_{10}$. This mixture was heated to reflux overnight, at which time IR spectroscopy showed no $Mn_2(CO)_{10}$. The mixture was cooled to 50 °C, and the volatiles were removed in vacuo. The resulting solid was dissolved in heptane/toluene (1:1) and filtered. The volume of the resulting deep red solution was reduced by 75%, several volumes of heptane were added, and the solution was cooled to dry-ice temperature. This gave **1** as a crystalline solid, which was filtered, washed (cold heptane), and dried in vacuo, yield after purification 4.35 g (4.33 mmol, 73%). IR (CS2 solution) carbonyl region: 1995 (w), 1920 (s), 1889 (ms) cm^{-1}. ^{1}H NMR (C6D6 solution): δ 2.02 (q, PCH_2CH3), 1.05 (q, PCH2CH_3). ^{31}P NMR (C6D6 solution): δ 47.12

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Table II. Positional Parameters and Their Estimated Standard Deviations

atom	x	y	z	B, Å^2
Te	0.57899 (4)	0.45914 (4)	0.2995 (2)	3.320 (8)
Mn	0.49380 (7)	0.36044 (7)	0.11821 (4)	2.26 (2)
P1	0.3936 (1)	0.2636 (1)	0.06016 (8)	2.88 (3)
P2	0.5991 (1)	0.4428 (1)	0.18013 (7)	2.86 (3)
C1	0.5944 (5)	0.2694 (5)	0.1067 (3)	3.1 (1)
O1	0.6587 (4)	0.2145 (4)	0.0996 (2)	4.7 (1)
C2	0.4354 (5)	0.3019 (5)	0.1765 (3)	3.1 (1)
O2	0.3944 (4)	0.2661 (5)	0.2149 (2)	5.0 (1)
C3	0.4056 (5)	0.4649 (6)	0.1210 (3)	3.4 (1)
O3	0.3501 (4)	0.5292 (5)	0.1255 (3)	5.7 (1)
C4	0.3547 (7)	0.1430 (6)	0.0919 (4)	4.9 (2)
C5	0.4436 (8)	0.0760 (7)	0.1088 (5)	7.0 (3)
C6	0.2701 (6)	0.3139 (7)	0.1088 (5)	7.0 (3)
C7	0.1969 (6)	0.3216 (9)	0.0892 (4)	6.3 (3)
C8	0.4503 (6)	0.2286 (7)	-0.0083 (3)	4.6 (2)
C9	0.3914 (8)	0.1505 (8)	-0.0435 (4)	6.2 (2)
C10	0.6089 (6)	0.3825 (6)	0.2503 (3)	4.0 (2)
C11	0.6490 (6)	0.2731 (6)	0.2476 (4)	4.6 (2)
C12	0.7316 (5)	0.4536 (7)	0.1578 (3)	4.2 (2)
C13	0.8035 (7)	0.4998 (8)	0.2025 (4)	5.9 (2)
C14	0.5649 (7)	0.5698 (6)	0.2041 (3)	4.5 (2)
C15	0.5744 (8)	0.6510 (6)	0.1576 (4)	5.6 (2)

ᵃ The form of the isotropic equivalent thermal parameter B is defined as $^4/_3[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab\beta(1,2) + ac\beta(1,3) + bc\beta(2,3)]$.

downfield from PPh₃ (br s, $\Delta\nu_{1/2} = 49$ Hz). UV–vis (near-UV–vis; Et₂O solution): λ 342 nm (ϵ_{max} 9700 M⁻¹ cm⁻¹), 450 (ϵ_{max} 3200). Anal. Calcd for C₃₀H₆₀Mn₂O₆P₄Te₂: C, 35.83; H, 6.01. Found: C, 36.79; H, 6.18. This material is slightly air-sensitive as a solid, much more so in either Et₂O or heptane solution. It is quite soluble in most organic solvents.

X-ray Structural Determination. Crystal data and some details of data collection and refinement are summarized in Table I. Single crystals suitable for X-ray analysis were grown by slow cooling (room temperature to -20 °C) of a solution of 1 in heptane/toluene (4:1, v/v). The crystals thus obtained were very large, up to ca. 5 mm; a roughly cubic fragment, ca. 0.2 mm on an edge, was cleaved from a larger crystal. The crystal was mounted with epoxy on a glass fiber. Protecting the crystal from air was unnecessary.

The data set was collected at room temperature on an Enraf-Nonius diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). The intensities of three check reflections were measured every 3 h during data collection; no significant decay was observed. Intensity data collected for six reflections as a function of the azimuthal setting angle ψ were found to vary less than 2% in intensity with ψ, so no absorption correction was made.
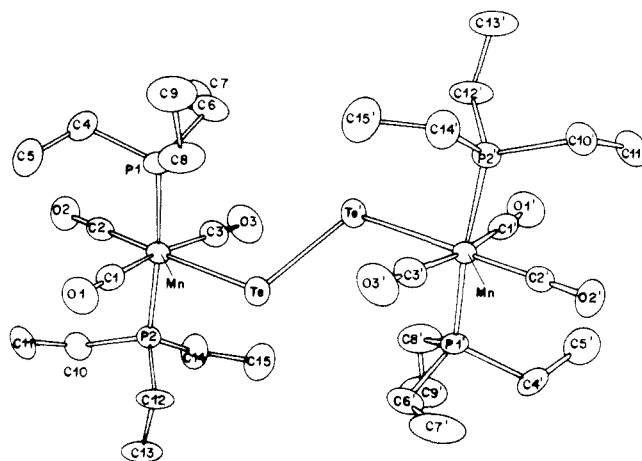
Data were corrected for Lorentz and polarization factors. Intensities were considered observed if $I > 3\sigma(I)$. The computer programs used were part of the Enraf-Nonius SDP package. The structure was solved with a combination of Patterson and Fourier methods. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were not included in the model, as their contribution to the overall scattering was minimal and their positions were of no structural interest, although their positions were clearly evident in a final Fourier difference map. The final atomic coordinates and their estimated standard deviations are shown in Table II.

Pyrolysis of 1. A Schlenk tube was charged with a purified sample of 1 (0.49 g, 0.49 mmol), evacuated, and closed. The sample was then heated to 300 °C. The solid first melted to an oil, then evolved gas, and finally formed a shiny metallic powder. During the pyrolysis the vessel was periodically opened to vacuum. This removed the gaseous byproducts of the reaction. After 16 h the vessel was evacuated further to remove all traces of the organic products, and the vessel was cooled. The black solid was extracted with diethyl ether, isolated by filtration, and dried; yield 0.17 g (95%). The X-ray diffraction powder pattern showed MnTe as the only solid-state product of this reaction.

Results

Preparation of Manganese Telluride. The reaction of Mn₂(C-O)₁₀ with 2 equiv of Et₃PTe in refluxing toluene⁵ yields a deep red-brown solution from which a crystalline red-brown solid

Figure 1. Projection of the molecular structure of 1.

Table III. Selected Bond Distances and Angles in Compound 1 (Estimated Standard Deviations in Parentheses)

Distances, Å			
Mn–Te	2.7175 (11)	Mn–C3	1.826 (7)
Mn–P1	2.312 (2)	Te–Te′	2.7628 (7)
Mn–P2	2.308 (2)	C1–O1	1.140 (9)
Mn–C1	1.832 (7)	C2–O2	1.164 (9)
Mn–C2	1.766 (7)	C3–O3	1.140 (9)

Angles, deg			
Mn–Te–Te′	105.50 (3)	P1–Mn–C2	87.7 (2)
Te–Mn–P1	93.31 (6)	P1–Mn–C3	94.5 (2)
Te–Mn–P2	90.06 (6)	P2–Mn–C1	88.0 (2)
Te–Mn–C1	84.4 (2)	P2–Mn–C2	89.1 (2)
Te–Mn–C2	177.1 (2)	P2–Mn–C3	90.2 (2)
Te–Mn–C3	85.7 (2)	C1–Mn–C2	98.3 (3)
P1–Mn–P2	174.41 (8)	C1–Mn–C3	170.0 (3)
P1–Mn–C1	87.8 (2)	C2–Mn–C3	91.5 (3)

compound can be isolated and readily purified by crystallization. The solid is pyrolyzed in a sealed tube under vacuum at 300 °C. Gas is evolved as the solid first melts and then decomposes. Manganese telluride (MnTe) is the only observed solid product. (The volatile products of this pyrolysis were not analyzed.) These results are summarized in eq 1.

$$(CO)_{10}Mn_2 + 2Et_3PTe \rightarrow 1 \rightarrow MnTe \qquad (1)$$

Isolation and Characterization of [(Et₃P)₂(CO)₃MnTe]₂ (1). We have characterized the intermediate complex 1. The ¹H NMR spectrum of this compound shows two quintets (δ 2.02, 1.05). Qualitatively, this spectrum is identical with that of (Et₃P)₂-(CO)₃MnBr and is characteristic of a metal complex having coordinated PEt₃. The ³¹P NMR spectrum of 1 shows a single broad resonance (δ 47.12 downfield from PPh₃, $\Delta\nu_{1/2} = 49$ Hz). This spectrum is also qualitatively identical with that of (Et₃P)₂(CO)₃MnBr. The ³¹P resonance of neither compound is affected by added free PEt₃; thus, the breadth of the resonances is due entirely to the interaction with the quadrupolar Mn nucleus.⁶

The infrared spectrum of 1 shows bands in the carbonyl stretching region at 1995 (w), 1920 (s), and 1889 cm⁻¹. This pattern is well documented for complexes of the form *trans*-L₂-(CO)₃MnX (L = donor ligand, X = halide), and the bands have been unambiguously assigned.⁷ The near-UV–visible absorption spectrum of 1 shows two prominent peaks (λ 342 nm (ϵ_{max} 9700 M⁻¹ cm⁻¹), 450 (ϵ_{max} 3200)). The intense color of the material is obvious from the high extinction coefficients.

We have determined the crystal and molecular structure of 1 by single-crystal X-ray diffraction. The molecular structure is shown in Figure 1; selected bond distances and angles are listed in Table III. (The bond distances and angles associated with

(5) This reaction is carried out in the presence of a large excess of PEt₃ (a total of 4.6 equiv of PEt₃/Te atom). Phosphinetellurides are in active equilibrium with free phosphine and elemental tellurium.⁹ The excess phosphine was added to avoid possible difficulty due to the intrusion of this equilibrium into the insertion reactions of interest.

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the ethyl groups of the triethylphosphine ligands are unremarkable and are omitted in the interest of brevity.) The molecule is a dimer whose halves are related by an inversion center. The manganese atoms have a distorted octahedral coordination and are bridged by a ditelluride unit. The two phosphine ligands are trans, and the three carbonyls have a *mer* configuration. The carbonyls show essentially linear coordination to manganese (average Mn–C–O angle 177.5°). Mn, Te, C2, O2, and their symmetry equivalents lie approximately in a plane; the other ligands are arranged such that this plane nearly bisects the P1–Mn–C3 and P2–Mn–C1 angles. The Mn–P distances are typical of manganese(I) phosphine complexes.[8a-f] Two distinct kinds of Mn–C distances are seen. The longer distance (exemplified by Mn–C1 at 1.832 (7) Å and Mn–C3 at 1.827 (7) Å) is typical of Mn–C distances for carbonyls trans to π-bonding ligands such as carbonyls or phosphines. The shorter Mn–C distance (Mn–C2 at 1.766 (7) Å) is comparable to Mn–C distances observed for carbonyls trans to strong σ-bonding ligands such as SCN,[8f] Br,[8b] or acetate.[8c]

The most remarkable feature of the complex is the ditelluride bridge. The structure is that of a typical diorganoditelluride[9] with two differences: (1) The organic termini of the typical organic ditelluride are replaced with $(Et_3P)_2(CO)_3Mn$ moieties. (2) The R–Te–Te–R dihedral angle is 180° rather than ca. 90°.

Discussion

The process described by eq 1 is a very mild route to the solid-state compound MnTe, which is formed as a microcrystalline powder in essentially quantitative yield. This procedure is much more expedient than the preparation from the elements, which has previously appeared,[10] requiring reaction at 800° followed by long-term annealing at 500°. Inasmuch as both $Mn_2(CO)_{10}$ and Et_3PTe (or, moreso,[3] Me_3PTe) are volatile, this method may also be adaptable to the production of thin films by vapor-phase epitaxy (VPE).

The isolation and characterization of the complex 1 is significant, showing that phosphine tellurides are convenient synthesis equivalents of atomic tellurium in organometallic synthesis. The phosphine dissolves elemental tellurium[11] and in that way enhances the reactivity of the metal. Reactions that occur only slowly with elemental tellurium should be much faster with R_3PTe.

The nature of 1 is important in relation to the synthesis of solid-state materials. A critical problem in the preparation of electronic materials using organometallic sources and reactions has been the incorporation of impurities from the organic ligands on the source compounds. Primarily, this is due to the nature of the ligands, which tend to be organic radicals (e.g. the methyl radicals in $GaMe_3$ and $AsMe_3$ in the formation of GaAs by VPE). In the present case, the organic ligands that stabilize 1 are not radicals but stable, volatile molecules. Pyrolysis of 1 generates no reactive radicals that can be incorporated in the growing solid. It is also important to note that the process in eq 1 forms MnTe without the intermediacy of atomic Mn and/or Te. It is therefore not necessarily the case that the best organometallic source for a given element is a compound that unimolecularly decomposes to give that element. Organometallic reactions can be exploited before the deposition/decomposition occurs.

The characterization of 1 is also significant because there are no reported cases of a bridging Te_2 unit of this type in an organometallic complex. There are several reports of μ-Te_2 complexes, but these generally show the Te_2 unit bridging the M_2 unit

in a perpendicular fashion.[12] The structure of 1 clearly shows a simple "organic" ditelluride and should be compared to [Cp-$(CO)_2MnSe]_2$,[13] the only reported organometallic analogue of an organic diselenide. There is a very recent report of a rather different μ-Te_2 array in which the Te_2 unit is asymmetrically placed with respect to two Re centers.[14] It is intriguing to compare that case to the present one.

Several features of the structure of 1 are noteworthy. The Te–Te bond is longer in 1 than in an organic ditelluride[9] (2.763 vs 2.715 Å in bis(4-methoxyphenyl)ditelluride (2)). Similarly, the Mn–Te–Te angle in 1 is slightly larger than the C–Te–Te angle in a typical organic ditelluride (105.5° vs 99.8° in 2). Both of these items, as well as the 180° dihedral angle in 1, are explained by the steric bulk of the $(Et_3P)_2(CO)_3Mn$ group. Comparison of the Mn–Te bond length in 1 with M–Te lengths in known metal–telluride complexes shows them to be in the expected range for a Mn–Te single bond.

We rationalize the formation of 1 from $Mn_2(CO)_{10}$ and Et_3PTe as a sequence of insertion reactions (eq 2). There are two related

$$\text{MnMn} \xrightarrow{\text{R}_3\text{PTe}} \text{MnTeMn} \xrightarrow{\text{R}_3\text{PTe}} \text{MnTeTeMn} \qquad (2)$$
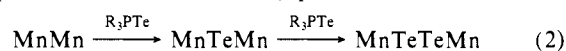
reports in the literature. duMont has shown that the reaction of R_2PSiMe_3 with elemental tellurium gives $R_2PTeSiMe_3$, presumably via the corresponding phosphine telluride.[15] Also, recent results from our laboratory have shown that HgTe can be formed by the reaction of HgR_2 with phosphine tellurides.[2] We have suggested the insertion of atomic tellurium into the metal–carbon bonds of HgR_2 as a crucial step in the formation of HgTe. In the present work we have extended the insertion reaction to include metal–metal bonds. This result is also interesting in that not one but two tellurium atoms have been inserted into the Mn–Mn bond. Not only is the double insertion a new process, but also it is curious because it is well-known that S (Se) can easily be removed from organic disulfides (diselenides) by treatment with basic phosphines.[16] Moreover, in several cases the removal of S or Se from organometallic disulfides or diselenides by phosphines has been observed.[13,17] Apparently, in the present case the reverse reaction dominates. This can be rationalized by recalling that when purified, the (trialkylphosphine)telluride is thermally unstable,[11] depositing tellurium from solution at ca. 70 °C. This is not observed for R_3PS or R_3PSe, making it clear that the P–Te bond is weaker than the P–S and P–Se bonds in the respective phosphine chalcogenides. Therefore, the driving force for removal of Te from a ditelluride (the formation of a P–Te bond) is weaker than that in the corresponding disulfide or diselenide.

The ability of the phosphinetelluride to provide a tellurium atom, which is capable of insertion into covalent bonds, is noteworthy. It is reasonable to describe the phosphinetelluride as a complex between the electron donor, triethylphosphine, and the electron acceptor, atomic tellurium. The atomic tellurium in this complex is functionally in an excited-state configuration, specifically a combination of the ^1D and ^1S states of the atom.[18] It is known that S and Se atoms react in the vapor phase with hydrocarbons to give direct insertion into C–H bonds,[19] and it has been observed that these insertion reactions occur only if the

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chalcogenide atoms are in the ¹D or ¹S states. While the analogous reaction for Te atoms has not been studied, it is reasonable to expect that similar reactions will occur. We suggest that (trialkylphosphine)tellurides are acting as sources of tellurium which is effectively in an excited atomic state and therefore capable of the observed insertion reactions.

The replacement of 4 equiv of CO by triethylphosphine, which occurs during the formation of **1**, has ample precedent.[4,20] It is known that $(CO)_5MnBr$ reacts with PR_3 (R = alkyl, alkoxide) at 37 °C to give *cis*-$Mn(CO)_3(PR_3)_2Br$ and that this complex isomerizes at 60 °C to the trans isomer. The conditions of formation of **1** are more vigorous, and therefore the ligand replacement proceeds to completion.

In view of the structure of the intermediate **1** the pyrolysis to give MnTe is easily explained. Heating simply removes the labile and volatile two-electron ligands CO and Et_3P. This is analogous to the very well-known decomposition of binary metal carbonyl[21]

complexes to give the metal and CO; however, in this case the inorganic nucleus of the complex is bimetallic. It is quite important that this decomposition yields only MnTe. There are other stable phases in the Mn–Te phase diagram, namely Mn, Te, and $MnTe_2$. The fact that none of these are observed to contaminate the solid-state product argues that the stoichiometry of the product is set not only by the stoichiometry of the starting material but also by the nature of the decomposition reaction.

Conclusions

We have discovered a mild method for preparing MnTe using organometallic reagents. The treatment of manganese carbonyl with 2 equiv of (triethylphosphine)telluride in refluxing toluene gives $[(PEt_3)_2(CO)_3MnTe]_2$, which we have isolated and characterized. Subsequent vacuum pyrolysis of this complex yields MnTe as the only nonvolatile product. The structure of **1** and a mechanistic route from starting materials to this intermediate have been discussed.

Supplementary Material Available: Table of thermal parameters (1 page); table of observed and calculated structure factors (29 pages). Ordering information is given on any current masthead page.

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Mechanistic Investigation of the ZrMe/PtMe Exchange in Cp*ZrMe(μ-OCH₂Ph₂P)₂PtMe₂

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Abstract: The coordinatively unsaturated heterobimetallic, *cis*-Cp*Zr(CH₃)(μ-OCH₂Ph₂P)₂Pt(CH₃)₂ (**2a**, Cp* = η⁵-C₅Me₅), synthesized via alcoholysis of Cp*ZrMe₃ by *cis*-(HOCH₂Ph₂P)₂PtMe₂ (**1a**), manifested an intermetallic exchange of Me groups through labeling studies. Thermolysis of Cp*Zr(CD₃)(μ-OCH₂Ph₂P)₂Pt(CH₃)₂ (**2a-Zr-d₃**) produced Cp*Zr(CH₃)(μ-OCH₂Ph₂P)₂Pt(CH₃)(CD₃) (**2a-Pt-d₃**), as monitored by ¹H NMR. ¹⁹⁵Pt NMR crossover experiments utilizing NMR isotope shifts revealed that a scrambling process engendered the concurrent formation of all remaining isotopomers (**2a**, **2a-d₉**, **2a-Zr-d₃/Pt-d₃**, **2a-Pt-d₆**). The rate of crossover, measured by thermolysis of **2a** and **2a-d₉**, was equivalent to the rate of ZrMe/PtMe exchange. From a series of labeling, kinetics, and crossover studies, some involving *cis*-Cp*Zr(CH₃)(μ-OCH₂CH₂Ph₂P)₂Pt(CH₃)₂ (**2b**) isotopomers, a mechanism for the overall process is presented. A combination of intramolecular ZrMe/PtMe exchange (k_1) and bimolecular ZrMe/ZrMe scrambling (k_2) reactions comprise the most probable pathway. A kinetic model, derived from specific NMR experiments and checked via simulations, depicts k_1 as the rate-determining step. Activation parameters ($\Delta H^* = 29.6 \pm 1.0$ kcal/mol, $\Delta S^* = -5 \pm 3$ eu) may be reconciled by envisioning either five or four (requiring phosphine dissociation) coordinate $(\mu\text{-CH}_3)_2$ transition states/intermediates. Coordinatively saturated Cp*Zr(CH₃)₂(μ-OCH₂Ph₂P)(CD₃)₂RhCp* (**5-Rh-d₆**) does not undergo Me exchange prior to or during decomposition. Factors contributing to Me transfer, alternative mechanisms, and the relevance of these homogeneous alkyl exchanges to similar heterogeneous processes are discussed.

Heterogeneous catalysts responsible for the making and breaking of C–C and C–O bonds are usually comprised of electron-rich metals deposited on a Lewis acidic metal oxide support.[1,2] The role of the latter cocatalyst ranges from serving as a dispersive medium to one of extensive involvement. In the latter extremes, strong metal support interactions (SMSI) of late metal/early metal oxide catalysts strongly suggest that the components may function in a cooperative fashion.[3] In these instances, the interface between metal oxide and late metal may determine the course of catalytic activity.[4] Late metals and corresponding oxides[5] have exhibited dramatically different reactivity, suggesting that the direct involvement of metal oxides as cocatalysts merits strong consideration.

If early metal oxide supports are reactive, the migration of surface groups across the heterogeneous interface may be critical

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