data for the dimeric structure show a doublet (proton decoupled, J_{PP} = 39.7 Hz)[15] at δ 89.08 ppm relative to external H_3PO_4. While the ^{31}P NMR spectrum of the dimeric compound was taken, it slowly decomposed and some precipitate was seen in the NMR tube. A new peak appeared at δ −12.40 ppm and grew with time. The new peak might be due to the liberation of free dppe. The ^1H NMR spectrum shows one singlet for the $-CH_2-$ units, centered at δ 2.63 ppm.

Complex 1 undergoes substitution reactions, as expected. The substituted products are stable in the solid state but unstable in solution. Complex 1 would be a versatile starting material for a wide range of complexes.

Acknowledgment. We thank Dr. J. H. Jeong for the X-ray crystal structure determination. Financial support from the Korea Science and Engineering Foundation is gratefully acknowledged.

Supplementary Material Available: Tables of anisotropic thermal parameters and of cell dimensions and symmetry operations (2 pages); a table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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First Example of an Organogallium Compound Containing a Gallium–Tellurium Bond: Synthesis, Properties, and Molecular Structure of $[(Me_3CCH_2)_2GaTePh]_2$

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Summary: The first example of an organogallium compound with a Ga–Te bond, $[(Me_3CCH_2)_2GaTePh]_2$, which is stable at room temperature, has been synthesized and characterized by elemental analyses, IR, ^1H NMR, and ^{125}Te NMR spectroscopies, and an X-ray structural study. The dimeric molecule crystallizes in the monoclinic space group $P2_1/c$ with unit cell dimensions of a = 18.864 (7) Å, b = 10.041 (5) Å, c = 19.869 (9) Å, β = 101.80 (3)°, V = 3684 (5) Å^3, Z = 4, D_{calcd} = 1.505 g cm^{-3}, R = 0.030, and R_w = 0.035. The four-membered Ga_2Te_2 ring has a butterfly arrangement with the phenyl groups in the anti position relative to the ring. The Ga–Te bond distances are in the range 2.7435 (8)–2.7623 (8) Å.

Organometallic compounds of gallium with bonds to group 15 elements such as $R_3Ga{\cdot}ER'_3$[2] (E = N, P, As) and $(R_2GaER'_2)_2$[3] (E = P, As) have been receiving increasing attention due to their potential usefulness as precursors for the preparation of films of group 13–15 materials.[4] In contrast, similar types of compounds with bonds to the heavier group 16 elements have been the subject of only limited research. The early work of Coates[5] revealed that $GaMe_3$ reacted with EMe_2 (E = Se, Te) to form 1:1 adducts that were extensively dissociated in the vapor phase. Thus, the simple adduct $Me_3Ga{\cdot}TeMe_2$ is the only example of a reported compound containing a Ga–Te bond prior to the present work. When selenols[6] were used, elimination reactions occurred at room temperature and dimeric derivatives of the type $(Me_2GaER)_2$ (E = Se; R = Me, Ph) were formed. These dimers were stable to dissociation in the gas phase at moderate temperatures, but the gallium–chalcogen bond was cleaved by NMe_3 to give monomeric species of the type $Me_2GaER{\cdot}NMe_3$.[6] The only other examples of derivatives containing Ga–Se bonds are $[Et_2GaSe(SiEt_3)]_28$[7] $[i\text{-}Pr(Br)GaSeEt]_3$,[8] and $(EtGaSe)_n$.[7]

Table I. Interatomic Distances (Å) for $[(Me_3CCH_2)_2GaTePh]_2$

(A) Gallium–Tellurium Distances			
Ga(1)–Te(1)	2.7623 (8)	Ga(2)–Te(2)	2.7525 (8)
Ga(1)–Te(2)	2.7435 (8)	Ga(2)–Te(1)	2.7623 (8)
(B) Gallium–Carbon Distances			
Ga(1)–C(7)	1.975 (7)	Ga(2)–C(23)	1.988 (7)
Ga(1)–C(12)	1.962 (8)	Ga(2)–C(28)	1.979 (8)
(C) Tellurium–Carbon Distances			
Te(1)–C(1)	2.125 (6)	Te(2)–C(17)	2.125 (6)

The first example of an organometallic gallium–tellurium compound, $(Me_3CCH_2)_2GaTePh$, which is not a simple adduct, has been prepared by the reaction of $Ga(CH_2CMe_3)_2Cl$ with LiTePh in Et_2O:

$$Ga(CH_2CMe_3)_2Cl + LiTePh \xrightarrow{Et_2O} (Me_3CCH_2)_2GaTePh + LiCl$$

The new compound has been fully characterized by partial elemental analyses (C and H), physical properties, infrared spectroscopy, ^1H and ^{125}Te NMR spectroscopies, and an X-ray structural study. The tellurium reagent[9] LiTePh

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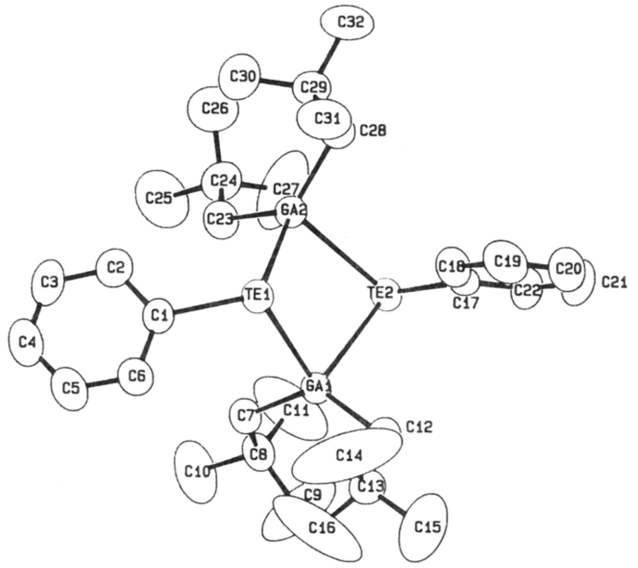

Figure 1. ORTEP plot of $[(Me_3CCH_2)_2GaTePh]_2$. The thermal ellipsoids were drawn at the 40% probability level.

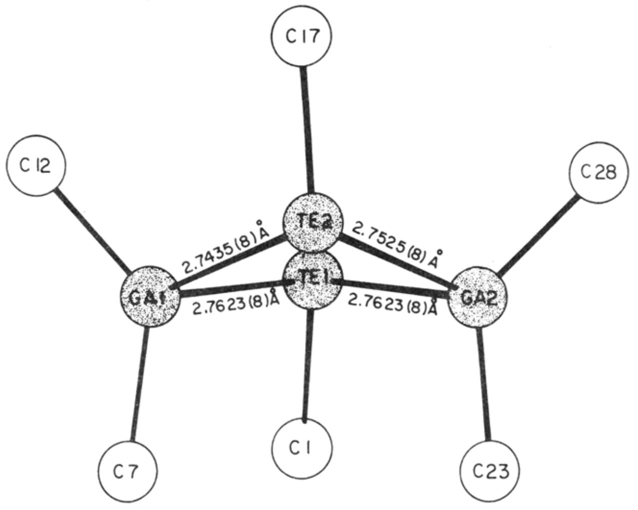

Figure 2. Geometry of the Ga_2Te_2 ring in $[(Me_3CCH_2)_2GaTePh]_2$.

was generated by the reductive cleavage of Te_2Ph_2 by $LiBEt_3H$ in THF/Et_2O. The use of a slight excess of Te_2Ph_2, which was readily removed by washing the LiTePh with pentane, ensured that no $LiBEt_3H$ would be available to react with $Ga(CH_2CMe_3)_2Cl$ in the second step of the synthesis. The reagent $LiBEt_3H$ has been observed previously to ethylate $GeCl_4$.[10] The product $(Me_3CCH_2)_2GaTePh$ was purified by repetitive low-temperature (−20 °C) crystallizations from pentane and was isolated in low yield (20%) as an off-white, extremely air-sensitive solid. An unidentified orange, oily product, which was shown to contain tellurium by ^{125}Te NMR spectroscopy, prevented the isolation of the above product in higher yield.

The structure of $(Me_3CCH_2)_2GaTePh$ consists of discrete dimeric units with the formula $[(Me_3CCH_2)_2GaTePh]_2$. There were no abnormally close contacts between dimeric units in the unit cell. The labeling of the atoms in the molecule is shown in Figure 1. The geometry of the Ga_2Te_2 butterfly ring is depicted in Figure 2. The interatomic distances and angles are collected in Tables I and II.

Table II. Angles (deg) for $[(Me_3CCH_2)_2GaTePh]_2$

(A) Angles around the Gallium Atom			
Te(1)–Ga(1)–Te(2)	92.1 (2)	Te(1)–Ga(2)–Te(2)	91.92 (2)
Te(1)–Ga(1)–C(7)	103.5 (2)	Te(1)–Ga(2)–C(23)	104.4 (2)
Te(1)–Ga(1)–C(12)	111.6 (4)	Te(2)–Ga(2)–C(28)	114.2 (3)
Te(2)–Ga(1)–C(7)	108.9 (3)	Te(1)–Ga(2)–C(23)	103.7 (3)
Te(2)–Ga(1)–C(12)	103.7 (3)	Te(1)–Ga(2)–C(28)	105.8 (2)
C(7)–Gal(1)–C(12)	130.4 (4)	C(23)–Ga(2)–C(28)	129.7 (4)
(B) Angles around the Tellurium Atom			
Ga(1)–Te(1)–Ga(2)	83.51 (2)	Ga(1)–Te(2)–Ga(2)	84.04 (2)
Ga(1)–Te(1)–C(1)	102.6 (2)	Ga(1)–Te(2)–C(17)	99.1 (2)
Ga(2)–Te(1)–C(1)	106.8 (2)	Ga(2)–Te(2)–C(17)	103.8 (2)
(C) Gallium–Carbon–Carbon Angles			
Ga(1)–C(7)–C(8)	121.6 (5)	Ga(2)–C(23)–C(24)	121.3 (6)
Ga(1)–C(12)–C(13)	123.1 (6)	Ga(2)–C(28)–C(29)	122.7 (6)
(D) Tellurium–Carbon–Carbon Angles			
Te(1)–C(1)–C(2)	121.1 (5)	Te(2)–C(17)–C(18)	122.7 (5)
Te(1)–C(1)–C(6)	119.4 (5)	Te(2)C(17)–C(21)	118.2 (6)

The Ga–Te bond distances in $[(Me_3CCH_2)_2GaTePh]_2$ are in the range 2.7435 (8)–2.7623 (8) Å. The average Ga–Te bond of 2.755 Å is 0.14 Å longer than the sum of the Ga and Te covalent radii, 2.62 Å.[11] Although no molecular compounds that contain Ga–Te bonds have been structurally characterized, Ga–Te bond distances have been reported for four GaTe-based solid-state phases. The average Ga–Te bond distances for the solid-state phases GaTe (monoclinic),[12,13] GaTe (hexagonal),[14] and GaTeCl[15] are 2.665, 2.61, and 2.634 Å, respectively. The Ga_2Te_5 phase contains $GaTe_4$ tetrahedra with a Ga–Te bond distance of 2.641 Å.[3]

The four-membered ring in $[(Me_3CCH_2)_2GaTePh]_2$ has a butterfly arrangement as found in $[I_2GaS(i\text{-}Pr)]_2$.[16] The angle of fold about the gallium atoms in $[(Me_3CCH_2)_2GaTePh]_2$ is 150.21°, and that about the tellurium atoms is 148.01°. The angle of fold about the gallium atoms in $[I_2GaS(i\text{-}Pr)]_2$ is 143.3 (2)°.[16] Interestingly, the ring systems in the dimers $[Ph_2GaSEt]_2$[17,18] and $[I_2GaSMe]_2$[17,19] are planar. The phenyl groups in $[(Me_3CCH_2)_2GaTePh]_2$ are in the anti position relative to the ring. The methyl groups in $[I_2GaSMe]_2$[17,19] are also in the anti position relative to the planar ring, as are the ethyl groups in $[Ph_2GaSEt]_2$.[17,18] However, $[I_2GaS(i\text{-}Pr)]_2$, which has a butterfly ring geometry, has the isopropyl groups in the syn position.[16]

Each gallium and tellurium atom in $[(Me_3CCH_2)_2GaTePh]_2$ has a distorted-tetrahedral coordination environment. The Te–Ga–Te angles are 91.92 and 92.12°. These angles are similar to the S–Ga–S angles of 94.3° in $[I_2GaSMe]_2$, 93.6° in $[I_2GaS(i\text{-}Pr)]_2$, and 89.1° in $[Ph_2GaSEt]_2$.[17] The Ga–Te–Ga angles in $[(Me_3CCH_2)_2GaTePh]_2$ are 83.51 and 83.04°. These angles are similar to the Ga–S–Ga angles of 86.4° in $[Ph_2GaSEt]_2$, 85.6° in $[I_2GaSMe]_2$, and 84.7° in $[I_2GaS(i\text{-}Pr)]_2$.[16]

The NMR spectral properties of the new gallium–tellurium compound are consistent with the presence of di-

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Table III. Summary of Crystal Data and Refinement Parameters

formula	$(GaTeC_{16}H_{27})_2$
M_r	833.428
cryst syst	monoclinic
space group	$P2_1/c$
cell const at 23 (1) °C	
a, Å	18.864 (7)
b, Å	10.041 (5)
c, Å	19.869 (9)
β, deg	101.80 (3)
V, Å^3	3684 (5)
no. of molecules/unit cell (Z)	4
D_{calcd}, g cm^{-3}	1.505
cryst dimens, mm	0.18 × 0.25 × 0.38
abs coeff (μ(Mo Kα)), cm^{-1}	30.4
scan technique	$\omega-2\theta$
scan rate (in 2θ), deg min^{-1}	2.1–20
2θ limit, deg	46
hkl range	−20 to +20, 0 to +11, 0 to +21
no. of unique data measd	5100
no. of data used in refinement ($I > \sigma(I)$)	3954
no. of params	397
$R = \sum \|\|F_o\| - K\|F_c\|\|/\sum\|F_o\|$	0.030
$R_w = (\sum w(\|F_o\| - K\|F_c\|)^2/\sum wF_o^2)^{1/2}$	0.035
$S = [\sum w(\|F_o\| - K\|F_c\|)^2/(n_o - n_v)]^{1/2}$	0.94
wtg params ($w^{-1} = \sigma^2(F_o) + (PF_o)^2 + q$)	
P	0.02
q	1.0
scale factor, K	0.6497 (2)
max shift in final cycle (Δ/σ)	0.03
residual electron dens in final diff Fourier synth, e/Å^3	−0.33 to +0.44

Table IV. Positional Parameters (Esd's in Parentheses) for $[(Me_3CCH_2)_2GaTePh]_2$[a]

atom	x	y	z	B, Å^2
Te(1)	0.23526 (2)	0.46017 (4)	0.36194 (2)	4.466 (8)
Te(2)	0.19798 (2)	0.76885 (4)	0.23521 (2)	4.453 (8)
Ga(1)	0.21570 (3)	0.73101 (6)	0.37440 (3)	4.23 (1)
Ga(2)	0.27140 (3)	0.53118 (6)	0.23890 (3)	4.51 (1)
C(1)	0.3341 (3)	0.4253 (5)	0.4331 (3)	4.5 (1)
C(2)	0.3915 (4)	0.3614 (6)	0.4131 (3)	5.9 (2)
C(3)	0.4536 (4)	0.3314 (7)	0.4628 (4)	6.9 (2)
C(4)	0.4585 (4)	0.3626 (7)	0.5299 (4)	7.5 (2)
C(5)	0.4015 (4)	0.4245 (8)	0.5486 (4)	7.6 (2)
C(6)	0.3391 (4)	0.4567 (6)	0.5012 (3)	6.0 (2)
C(7)	0.3127 (3)	0.7953 (6)	0.4196 (3)	5.2 (1)
C(8)	0.3333 (3)	0.9419 (6)	0.4185 (3)	5.2 (1)
C(9)	0.2822 (5)	1.0242 (8)	0.4459 (7)	17.2 (4)
C(10)	0.4083 (5)	0.9634 (8)	0.4601 (5)	11.5 (3)
C(11)	0.3362 (6)	0.9864 (9)	0.3475 (5)	15.9 (3)
C(12)	0.1199 (3)	0.7718 (8)	0.3933 (3)	6.8 (2)
C(13)	0.0990 (3)	0.7417 (6)	0.4618 (3)	5.7 (2)
C(14)	0.0880 (7)	0.604 (1)	0.4688 (6)	25.1 (4)
C(15)	0.0313 (5)	0.807 (2)	0.4689 (5)	20.1 (5)
C(16)	0.1528 (6)	0.783 (2)	0.5171 (5)	24.7 (6)
C(17)	0.0874 (3)	0.7130 (6)	0.2050 (3)	4.8 (1)
C(18)	0.0615 (3)	0.5929 (6)	0.2226 (4)	6.1 (2)
C(19)	−0.0115 (4)	0.5641 (8)	0.2035 (4)	7.9 (2)
C(20)	−0.0573 (4)	0.6533 (9)	0.1660 (4)	8.7 (2)
C(21)	−0.0322 (4)	0.7726 (8)	0.1474 (5)	8.4 (2)
C(22)	0.0401 (3)	0.8023 (7)	0.1673 (4)	6.3 (2)
C(23)	0.3749 (3)	0.5842 (7)	0.2647 (3)	5.9 (2)
C(24)	0.4163 (3)	0.6338 (7)	0.2106 (4)	6.6 (2)
C(25)	0.4936 (4)	0.669 (1)	0.2451 (5)	12.3 (3)
C(26)	0.4235 (5)	0.517 (1)	0.1624 (5)	11.2 (3)
C(27)	0.3777 (5)	0.7415 (9)	0.1699 (5)	15.5 (3)
C(28)	0.2202 (4)	0.4281 (6)	0.1586 (3)	5.8 (2)
C(29)	0.2182 (4)	0.2763 (6)	0.1577 (3)	6.2 (2)
C(30)	0.2924 (5)	0.2199 (8)	0.1877 (5)	9.9 (3)
C(31)	0.1643 (5)	0.2253 (8)	0.1994 (4)	9.5 (2)
C(32)	0.1925 (5)	0.2272 (8)	0.0834 (4)	9.4 (2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

meric molecules $[(Me_3CCH_2)_2GaTePh]_2$ in solution. The ^{125}Te NMR spectrum, the most useful for identifying components, exhibits only one line at 345.4 ppm. For comparison, a solution of LiTePh in THF gave a line at 133.9 ppm, whereas the unknown impurity, which was an orange oil, had a line at 370.1 ppm. The ^{1}H NMR spectrum in benzene-d_6 had a broadened line at 1.30 ppm for the methylene protons of the neopentyl group and at least six lines of decreasing intensity from 1.11 to 0.81 ppm for the methyl protons of the neopentyl group. The phenyl lines were obscured by those due to the solvent. The occurrence of multiple and/or broadened lines for the neopentyl group protons suggests isomers, but their presence could not be confirmed. Since the X-ray structural study revealed only the trans isomer with the phenyl rings in the anti position relative to the ring, the gallium–tellurium bonds in the dimer must have broken at least partially for isomerization to have occurred.

Experimental Section

All compounds described in this investigation were extremely sensitive to oxygen and moisture and were manipulated in a standard vacuum line or under a purified argon atmosphere. The alkylgallium chloride $Ga(CH_2CMe_3)_2Cl$ was prepared and purified by literature methods.[20a] The reagent $LiBEt_3H$ (1.0 M in THF) was obtained from Aldrich Chemical Co., whereas Te_2Ph_2 was prepared as previously described.[20b] Solvents were dried by conventional procedures. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, NY. Infrared spectra of Nujol mulls between CsI plates were recorded by means of a Perkin-Elmer 683 spectrometer. Absorption intensities are reported with the abbreviations vs (very strong), s (strong), m (medium), w (weak), and sh (shoulder). The ^{1}H NMR spectra were recorded at 90 MHz by using a Varian EM-390 spectrometer. Proton chemical shifts are reported in δ units (ppm) and are referenced to $SiMe_4$ at δ 0.00 ppm and benzene at δ 7.13 ppm. The ^{125}Te NMR spectra were recorded at 94.70 MHz by using a Varian XLAA-300 spectrometer. The proton-decoupled ^{125}Te NMR spectra are reported relative to diphenyl telluride ($TePh_2$) at δ 688 ppm, which was referenced to external dimethyl telluride ($TeMe_2$) at δ 0.00 ppm. The samples were run unlocked, and the chemical shifts were measured by tube interchange. All samples for NMR spectra were contained in sealed NMR tubes. Melting points were observed in sealed capillaries.

Synthesis of $(Me_3CCH_2)_2GaTePh$. In a glovebox, a side-arm dumper was charged with 0.749 g of LiTePh (ca. 3 mmol), which had been prepared[9] from Te_2Ph_2 and $LiBEt_3H$ in THF/Et_2O, and connected to a two-neck round-bottom flask charged with 0.871 g (3.52 mmol) of $Ga(CH_2CMe_3)_2Cl$. Diethyl ether (50 mL) was vacuum-distilled into the reaction vessel, and the contents were warmed to ambient temperature with stirring. LiTePh was slowly added over a 5-min time period to the ether solution. The colorless solution slowly became yellow. The mixture was stirred 16 h, and Et_2O was removed by vacuum distillation. An orange oil remained in the flask. The vessel was fitted with a medium frit and a Schlenk receiving flask in the glovebox. Anhydrous pentane (20 mL) was distilled into the flask, and repetitive low-temperature crystallizations (−10 to −20 °C) provided 0.336 g (0.807 mmol, 22.9% yield) of an off-white solid, which was identified as $(Me_3CCH_2)_2GaTePh$. Recrystallization of $(Me_3CCH_2)_2GaTePh$ from pentane at −20 °C afforded crystallographic quality crystals. Data for $(Me_3CCH_2)_2GaTePh$ are as follows: mp 109.0–110.5 °C dec (sample begins to decompose and darken at 96 °C and melts to an orange liquid at 109.0–110.5 °C); ^{1}H NMR (C_6D_6, δ) 0.81, 0.89, 0.96, 1.01, 1.05, 1.11 (s, combined lines, 18 H, $-CMe_3$), 1.30 (s, 3.7 H, $-CH_2-$); ^{125}Te{^{1}H} NMR (C_6D_6, δ) 345.4 (s). The ^{125}Te NMR spectrum of the orange oil from the reaction gave a reso-

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nance in the $^{125}Te\{^1H\}$ NMR spectrum at 370.1 ppm. The ^{125}Te NMR spectrum of a sample of LiTePh in THF gave a resonance in the $^{125}Te\{^1H\}$ NMR spectrum at 133.9 ppm. Anal. Calcd for $C_{32}H_{54}Ga_2Te_2$: C, 46.12; H, 6.53. Found: C, 46.41; H, 6.63. IR (Nujol, cm^{-1}): 3070 (vw), 3055 (vw), 1571 (m), 1430 (m), 1358 (m), 1232 (m), 1133 (m), 1099 (m), 1062 (vw), 1055 (vw), 1011 (m), 999 (w, sh), 994 (m), 795 (vw, br), 740 (w), 720 (s), 648 (w), 618 (m), 449 (w).

Crystallography. A colorless crystal of $(Me_3CCH_2)_2GaTePh$ was selected and sealed in a glass capillary under an argon atmosphere for examination by X-ray diffraction procedures. Data were collected on an Enraf-Nonius CAD-4 diffractometer by using graphite-monochromated Mo Kα radiation. Table III summarizes the unit cell data and the refinement parameters. Unit cell dimensions were determined by least-squares refinement of 25 reflections ($20.0° < 2\theta < 26.8°$). Three standard reflections were remeasured after every 1 h of X-ray exposure. The data were corrected for a slow, steady decrease of intensity over time. The maximum correction was 1.230 on I. An empirical absorption correction[21] was applied. Correction factors ranged from 0.85 to 1.31.

The structure of $(Me_3CCH_2)_2GaTePh$ was solved by direct methods with use of MULTAN 11/82.[22] An E-map phased with the best phase set gave the four heavy-atom positions. Subsequent difference electron density maps allowed location of the remaining atoms. All hydrogen atoms were included in the refinement, except that those on methyl groups were fixed at calculated positions riding on the parent carbon atoms. Positional parameters, excluding those for the hydrogen atoms, are given in Table IV.

Acknowledgment. This work was supported in part by the Office of Naval Research and by a generous grant from Eastman Kodak Co.

Supplementary Material Available: Tables of refined temperature factors for $[(Me_3CCH_2)_2GaTePh]_2$, hydrogen atom positional parameters, and carbon–carbon bond distances and angles (7 pages); a table of structure factors (29 pages). Ordering information is given on any current masthead page.

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Substituted Cyclopentadienyl Phosphinomethyl Complexes of Zirconium. Synthesis, Chemical Characteristics, Complexation with Rhodium Complexes, and Catalytic Properties. Molecular and Crystal Structure of $(\eta^5\text{-}t\text{-}BuC_5H_4)_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$†

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Summary: The synthesis of $Cp'_2Zr(CH_2PPh_2)_2$ (**1**) and $Cp'_2ZrCl(CH_2PPh_2)$ (**2**) ($Cp' = \eta^5\text{-}t\text{-}BuC_5H_4$) is reported. The ^1H NMR spectrum of **2** shows four separate ring proton absorptions, unambiguously assigned by decoupling experiments and simulated spectra. Reduction of **2** with Na/Hg produces a paramagnetic Zr(III) species formulated as $Cp'_2\overline{Zr(CH_2P}Ph_2)$ (**3**). Reduction of **1** with sodium naphthalenide leads to the monocyclopentadienyl $Cp'\overline{Zr(CH_2P}Ph_2)_2$ species **6** characterized by EPR features and simulated spectra. Evolution of **6** gives the hydridozirconium(III) species **7** able to hydrogenate, in a catalytic way, various olefins. Reactions of **1** with the cationic rhodium complex $Rh(COD)(PPh_3)_2BPh_4$ and the neutral dinuclear complex $Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_4$ produces the bimetallic complexes $Cp'_2Zr(CH_2PPh_2)_2[Rh(COD)]BPh_4$ (**8**) and $Cp'_2Zr(CH_2PPh_2)_2[Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2]$ (**9**), respectively. The X-ray structure of **9** was determined, giving the following crystal data: space group $P2_1/n$, a = 14.320 (2) Å, b = 19.488 (3) Å, c = 19.405 (2) Å, β = 95.08 (2)°, V = 5394 Å^3, Z = 4. The crystal structure displays relatively normal Zr and Rh geometric environments. Results for the catalytic hydroformylation of 1-hexene with **9** can be related to the t-Bu electronic effect.

We are interested in ((diphenylphosphino)methyl)zirconium and -titanium chemistry, and our previous results have shown that (i) the cyclometalated Zr(III) species $Cp_2\overline{Zr(CH_2P}Ph_2)$ ($Cp = \eta^5\text{-}C_5H_5$) (or $Cp\overline{M(CH_2P}Ph_2)_2$ with M = Ti, Zr) is an active precursor in the catalytic hydrogenation of olefins.[1,2] and (ii) d^0–d^8 [Zr,Rh] and [Ti,Rh] bimetallic systems,[3-7] synthesized due to the ability of the zirconium diphosphine (or titanium diphosphine) to complex rhodium compounds, were demonstrated to be efficient hydroformylation catalysts.[5,8-10]

The aim of the present work is to determine whether the introduction of an R group on the cyclopentadienyl ligand makes it possible to achieve a different catalytic behavior. We have focused our attention on new substi-

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† Dedicated to the memory of Professor D. Gervais.

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