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STUDIES ON MAIN GROUP METAL—TRANSITION METAL BONDED COMPOUNDS

II *. THE CRYSTAL AND MOLECULAR STRUCTURE OF π-$C_5H_5(CO)_3WGa(CH_3)_2$ AND EVIDENCE FOR MIXED ORGANOZINC AND ORGANOGALLIUM TRANSITION METAL DERIVATIVES

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Summary

Metal—metal derivatives of the general formula $(CH_3)_{3-x}GaTm_x$ (Tm = π-$C_5H_5(CO)_3Mo$, π-$C_5H_5(CO)_3W$) are obtained via reactions involving TmH and $(CH_3)_3Ga$ in methylcyclohexane. For $x = 1$ and $x = 3$ the species are prepared by the combination of reactants in the appropriate molar ratios. The derivatives represented by $x = 2$ may be obtained by heating the dimethyl derivatives under vacuum. NMR and IR data are presented for the molybdenum derivatives which show scrambling of the compounds in solution. Methyl exchange involving $(CH_3)_3Ga$ and $TmGa(CH_3)_2$ is very rapid but the analogous exchange involving Tm_2GaCH_3 is considerably slower. NMR evidence indicates that methyl exchange between Tm_2GaCH_3 and $TmGa(CH_3)_2$ is slow or non-existent and that exchange of Tm is slow on the NMR time scale.

The crystal structure of π-$C_5H_5(CO)_3WGa(CH_3)_2$ has been determined from single-crystal X-ray data. This compound crystallizes in space group $P2_1/n$ with four molecules per unit cell of dimensions $a = 8.707(2)$, $b = 10.928(3)$, $c = 13.04(3)$ Å and $\beta = 96.44(2)°$. Full-matrix least-squares refinement gave final discrepancy factors $R_1 = 0.075$ and $R_2 = 0.089$ for 1936 data having $I > 3\sigma(I)$.

Introduction

The structural and solution chemistry of organometallic compounds which contain both a transition metal moiety and a Group II or III metal are of considerable interest because of the recognized ability to form several species as a

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* For part I see ref. 1.

result of different types of bonding and because of the redistribution reactions which may occur.

During the past few years substantial progress has been made with regard to the solid state structures of many of these derivatives. These include a number of both symmetric and asymmetric species which contain metal—metal bonds. Structures of the following compounds serve as examples: $[\pi\text{-}C_5H_5(CO)_3Mo]_2Zn$ [1], $[\pi\text{-}C_5H_5(CO)_3MoZnClO(C_2H_5)_2]_2$ [1], $[\pi\text{-}C_5H_5(CO)_3MoZnBr \cdot 2\,THF]$ [2], $[(CO)_4Co]_2Hg$ [3], $[\pi\text{-}C_5H_5(CO)_3Mo]HgX$ (X = Cl, Br^-) [2], $[(CO)_4Co]_3In$ [4], and $[\pi\text{-}C_5H_5(CO)_3W]_3Ga$ [5]. In addition two rather unusual structures have been reported for the compounds $[H(\pi\text{-}C_5H_5)(\pi\text{-}C_5H_4)Mo]_2 \cdot Al_3(CH_3)_5$ and $[(\pi\text{-}C_5H_4)_2Mo]_2 \cdot [Al_2(CH_3)_3]_2$ [6] which contain both tetra- and penta-coordinated Al atoms bound to Mo atoms in bridging positions, C_5H_4 bridging groups, and bridging hydrogens in the former complex. The methyl groups are σ-bonded to the Al atoms and do not participate in multicenter bonding in these species.

The second group of compounds of interest to us contain bridging carbonyl groups between Group II or III metals and the transition metals. These are clearly illustrated by the structures of the magnesium compound $[\pi\text{-}C_5H_5(CO)_3Mo]_2\text{-}Mg \cdot 4$ pyridine [7] and the aluminum derivatives $[\pi\text{-}C_5H_5(CO)_3WAl(CH_3)_2]_2$ [8] and $[\pi\text{-}C_5H_5(CO)_3W]_3Al \cdot 3\,THF$ [9], but have not been reported for the heavier Group II or III metals.

Examination of the solution chemistry of the Group II and III metal—transition metal derivatives indicates that the mixed derivatives (TmMR, Tm = transition metal moiety of Mo, W, R = alkyl) of mercury can be formed but were unstable toward symmetrization [10—12], whereas for the derivatives of $Re(CO)_5^-$ no evidence was obtained for formation of the unsymmetrical species [13].

Examination of the Group III derivatives shows evidence for the formation of R_2TlTm (R = CH_3, C_6H_5; Tm = $C_5H_5(CO)_3M$; M = Mo, W) [14—16] but when Mays et al., attempted to prepare the mixed indium derivatives (Tm = $\pi\text{-}C_5H_5\text{-}(CO)_3M$, M = Mo, W; R = CH_3) they had no success [17]. Recently studies have appeared which indicate formation of the mixed $Tm_nGa(CH_3)_{3-n}$ species in solution with symmetrization to yield the crystalline Tm_3Ga derivative in the solid state [5].

We now wish to report both NMR and X-ray crystallographic studies which prove the formation of the mixed $Tm_nGa(CH_3)_{3-n}$ species and provide further details concerning their disproportionation reactions. We also provide evidence for the formation of the mixed $TmZnC_6H_5$ derivatives in solution.

Experimental

All preparations and subsequent manipulations were carried out under high vacuum conditions and/or under an argon or nitrogen atmosphere utilizing Schlenck tube and dry box techniques [18]. All solvents, with the exception of THF were dried over Na/K alloy and degassed prior to use. THF was dried over $LiAlH_4$. IR data were obtained on a Perkin—Elmer Model 267 Spectrometer and calibrated versus the 1601.4 cm^{-1} absorption of polystyrene film. NMR spectra were recorded on a Varian A 60A spectrometer operating at a probe temperature of 35°C unless otherwise noted. The cyclopentadienyl tricarbonyl hydrides of molybdenum and tungsten were prepared by reported procedures [19] and were doubly sublimed prior to use.

The dimethyl- and diethyl-zinc were prepared by standard techniques from the reaction of a Zn/Cu couple with the appropriate alkyl iodide [20]. Dimethylcadmium was prepared by the method of Gilman and Nelson [21]. These compounds were purified by distillation on the vacuum system with their purity determined from their NMR spectra. Diphenylzinc was prepared by reaction of diphenylmercury with zinc dust [22]. A similar reaction, the metal exchange, was used for preparation of trimethylgallium from gallium metal and dimethylmercury [23]. Molybdenum and tungsten hexacarbonyl were obtained from Pressure Chemical Co., and used as received.

Preparation of $[\pi\text{-}C_5H_5(CO)_3M]_2M'$ *derivatives*

The preparation of Zn and Cd derivatives indicated (M = Mo, W) were all performed by reaction of the transition metal hydride with either dimethylcadmium or diethylzinc according to the following reaction:

$$M'R_2 + 2\,TmH \rightarrow Tm_2M' + 2\,RH \qquad (1)$$

A typical reaction is described for the preparation of $[\pi\text{-}C_5H_5(CO)_3Mo]_2Zn$. $\pi\text{-}C_5H_5(CO)_3MoH$ (0.39 g, 1.6 mmol) was dissolved in 20 ml toluene in the reaction vessel which was then attached to the high vacuum line. Subsequently, diethylzinc (0.21 g, 1.7 mmol) was condensed into the vessel at —196°C. The vessel was then warmed slowly to room temperature. Gas evolution commenced in the temperature range of —10 to 0°C with the gas evolved identified as ethane from its mass spectrum. A cream colored precipitate formed concurrently with the evolution of ethane. The reaction mixture was stirred until gas evolution ceased (~5—10 min) at which time 1.57 mmol of ethane had been evolved as determined from pressure-volume measurements. The product was recovered by filtration and washed with 5 ml cyclopentane yielding in excess of 90% product. Similar procedures were used for the preparation of $[\pi\text{-}C_5H_5(CO)_3W]_2Zn$, $[\pi\text{-}C_5H_5(CO)_3Mo]_2Cd$, and $[\pi\text{-}C_5H_5(CO)_3W]_2Cd$ and gave yields of 80—90% recovered product with minimal effort. In all cases the IR spectra were in agreement with those obtained previously [24]. The analyses * of the products are (calc/found):

	C (%)	H (%)
$[\pi\text{-}C_5H_5(CO)_3Mo]_2Zn$	34.6/35.3	1.82/2.10
$[\pi\text{-}C_5H_5(CO)_3W]_2Zn$	26.3/25.5	1.38/1.45
$[\pi\text{-}C_5H_5(CO)_3Mo]_2Cd$	31.9/32.1	1.68/1.96
$[\pi\text{-}C_5H_5(CO)_3W]_2Cd$	24.7/25.1	1.30/1.58

Preparation of $\pi\text{-}C_5H_5(CO)_3MoGa(CH_3)_2$

$\pi\text{-}C_5H_5(CO)_3MoH$ (0.35 g, 1.42 mmol) was dissolved in methylcyclohexane (15 ml) and the reaction vessel attached to a high vacuum line. Trimethylgallium (0.163 g, 1.42 mmol) was condensed into the reaction vessel at —196°C. The vessel was sealed at a glass-constriction and heated at 90°C for 4 h. Over the course of the reaction period the color changed from the original pale yellow to

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* All analyses were performed by Schwartzkopf Microanalytical Laboratories, Woodside, New York.

an orange-yellow. Yellow crystals were deposited after 24 h at 0°C. The crystals were isolated via filtration followed by the rapid removal of solvent in vacuum. Prolonged exposure to vacuum resulted in symmetrization and loss of $Ga(CH_3)_3$ with formation of $[\pi\text{-}C_5H_5(CO)_3Mo]_2GaCH_3$. Addition of excess $\pi\text{-}C_5H_5(CO)_3MoH$ also leads to formation of $[\pi\text{-}C_5H_5(CO)_3Mo_2]GaCH_3$ but this compound was never isolated in pure form. The initial reaction appears to lead to quantitative elimination of methane, but the isolated product yield was variable due to the work-up procedure and potential redistribution reactions and was never determined. Analysis: Found: C, 34.1; H, 3.07. $\pi\text{-}C_5H_5(CO)_3MoGa(CH_3)_2$ calcd.: C, 34.8; H, 3.22%.

Preparation of $\pi\text{-}C_5H_5(CO)_3WGa(CH_3)_2$

In a manner completely analogous to the molybdenum hydride-trimethylgallium reaction $\pi\text{-}C_5H_5(CO)_3WH$ (0.572 g, 1.71 mmol) and trimethylgallium (0.196 g, 1.71 mmol) were combined and a yellow solid isolated. Analysis: Found: C, 27.4; H, 2.39. $\pi\text{-}C_5H_5(CO)_3WGa(CH_3)_2$ calcd.: C, 27.75; H, 2.57%.

Preparation of $[\pi\text{-}C_5H_5(CO)_3Mo]_3Ga$

$\pi\text{-}C_5H_5(CO)_3MoH$ (0.839 g, 3.41 mmol) was placed in a Pyrex reaction tube and attached to a vacuum line. Methylcyclohexane (~15 ml) and $(CH_3)_3Ga$ (0.132 g, 1.15 mmol) were condensed into the reaction vessel at −196°C. The vessel was sealed and heated at 120°C for 7 days. The initial pale yellow solution turned to an orange-yellow solution after 2-3 h and progressively turned a deep red over the remaining reaction period. A dark orange solid crystallized from solution after 5 days. The solid was isolated via filtration and washed with 5 ml of cyclopentane. Analysis: Found: C, 36.2; H, 2.11. $[\pi\text{-}C_5H_5(CO)_3Mo]_3Ga$ calcd.: C, 35.8; H, 1.88%.

Reactions monitored via NMR

Standard solutions of the molybdenum and tungsten hydrides and diphenylzinc in toluene were prepared separately. In a dry box, NMR tubes adapted for connection to a high vacuum line were loaded with reactants by calibrated syringe. Upon introduction of the second reactant the tube was frozen and maintained in this condition until the tube was evacuated and sealed. The tubes were subsequently rapidly warmed to room temperature, shaken and inserted in the NMR probe. The NMR signal resulting from the product C_5H_5 resonance was monitored with respect to intensity and position over the course of reaction time. Precise line positions were obtained by calibration with audio frequency sidebands. Concentrations were chosen so that all products remained in solution throughout the reaction period. Similar experiments with diphenylcadmium were not possible due to low solubility of cadmium compounds.

X-ray crystallographic study of $\pi\text{-}C_5H_5(CO)_3WGa(CH_3)_2$

Crystals were sealed in thin-walled glass capillaries under an N_2 atmosphere and mounted directly on a Syntex-$P2_1$ diffractometer. Although the crystals rapidly decomposed, one crystal, of dimensions ~0.15 × 0.20 × 0.95 mm without well-defined faces was sufficiently stable to allow data collection. The long axis was parallel to the capillary (ϕ) axis. Rotation and axial photographs and counter data established the monoclinic space group $P2_1/n$. Least-squares refinement of 15 reflections (Mo-K_α, $\lambda = 0.71069$ Å) yielded the cell data $a = 8.707(2)$, $b = 10.928(3)$, $c = 13.041(3)$ Å, $\beta = 96.44(2)°$, d(calc) = 2.316 g cm^{-3} for $Z = 4$. The non-conventional space group $P2_1/n$ was chosen to keep β close to 90° and thus reduce correlations between the x and z atomic coordinates. The corresponding conventional cell with symmetry $P2_1/c$ has cell parameters $a = 8.707$, $b = 10.928$, $c = 14.846$ Å, $\beta = 119.21°$. The transformation to the conventional cell is $\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 1 & 0 & 1 \end{bmatrix}$. The air-sensitivity and high reactivity of the compound prevented an experimental density determination.

Intensity data were collected with Mo-K_α radiation, which had been diffracted from a graphite monochromator in the parallel orientation. In view of the instability of the compound, a θ—2θ scan technique was used with scan rates varying with the peak intensities between 4.0° min^{-1} and 29.0° min^{-1}. The scans were from 2θ(Mo-K_{α_1}) — 1.0 to 2θ(Mo-K_{α_2}) + 1.0° with backgrounds measured at each end of the scan for a total time equal to one-half the scan time. Three standard reflections, measured after every 50 data, showed no systematic trends. Standard deviations were assigned [25] according to:

$$\sigma(I) = [\sigma^2_{\text{counter}} + (0.04\,I)^2]^{1/2}$$

where $\sigma_{\text{counter}} = (I + K^2B)^{1/2}$, I = net intensity, B = total background counts, and K is the ratio of scan time to background time. Of the 3405 data measured with $2\theta \leqslant 50°$, 1936 had $I \geqslant 3\,\sigma(I)$ and were used in the solution and refinement of the structures.

Solution of a three-dimensional Patterson synthesis [26] yielded the location of the tungsten and gallium atoms. Subsequent difference Fourier syntheses yielded the positions of the remaining non-hydrogen atoms. Anisotropic full-matrix least squares refinement [27,28] of all non-hydrogen atoms including anomalous scattering contributions [29] for tungsten and gallium atoms resulted in discrepancy factors of $\Sigma||F_0| - |F_c||/\Sigma|F_0| = 0.075$ and $[\Sigma w(|F_0| - |F_c|)^2/\Sigma w F_0^2]^{1/2} = 0.089$ with an error of fit $([\Sigma w||F_0| - |F_c||/(\text{NO-NV})]^{1/2})$ of 3.2. Table 1 contains a listing of atomic coordinates. The calculated and observed structure factors are available *. No absorption corrections were made due to the difficulty in establishing the macroscopic parameters of the crystal. The quality of the final parameters is thus clearly limited by significant absorption in this crystal.

Structure of π-$C_5H_5(CO)_3WGa(CH_3)_2$

The solid state structure of π-$C_5H_5(CO)_3WGa(CH_3)_2$ consists of discrete monomers. The labeling scheme, anisotropic thermal ellipsoids, and packing [30] are shown in Figs. 1, 2, and 3 respectively. Bond distances and angles are given in Table 2.

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* The Table of structure factors has been deposited as NAPS Document No. 02923. Order from ASIS/NAPS, c/o Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. A copy may be secured by citing the document number, remitting $5.00 for photocopies or $3.00 for microfiche. Advance payment is required. Make checks payable to Microfiche Publications. Outside of the U.S.A. and Canada, postage is $2.00 for a photocopy or $1.00 for a fiche.

TABLE 1

ATOMIC COORDINATES [a] FOR π-$C_5H_5(CO)_3WGa(CH_3)_2$ WITH ESTIMATED STANDARD DERIVATIONS OF THE LEAST SIGNIFICANT DIGIT IN PARENTHESES

	x	y	z
W	0.2174(1)	0.1890(1)	−0.0749(1)
Ga	0.5040(3)	0.1609(2)	−0.1331(2)
C1	0.2427(30)	0.2055(22)	−0.2246(23)
C2	0.0391(34)	0.0859(26)	−0.1272(19)
C3	0.3009(30)	0.0307(22)	−0.0451(15)
C4	0.5430(29)	0.0197(24)	−0.2261(18)
C5	0.6369(33)	0.3059(21)	−0.1179(20)
C6	0.3338(41)	0.3279(33)	0.0474(27)
C7	0.0825(47)	0.3639(28)	−0.0308(24)
C8	0.2117(69)	0.2489(39)	0.0967(21)
C9	0.2445(37)	0.3959(28)	−0.0294(21)
C10	0.0621(46)	0.2745(36)	0.0481(26)
O1	0.2382(27)	0.2184(21)	−0.3120(12)
O2	−0.0621(27)	0.0210(25)	−0.1602(19)
O3	0.3498(18)	−0.0701(13)	−0.0211(11)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
W	0.0151(2)	0.0086(1)	0.0040(1)	0.0026(1)	−0.0004(1)	−0.0002(1)
Ga	0.0157(4)	0.0084(3)	0.0046(1)	−0.0012(3)	−0.0000(2)	0.0003(1)
C1	0.0132(41)	0.0100(28)	0.0097(24)	0.0029(28)	0.0034(26)	0.0003(21)
C2	0.0199(54)	0.0125(33)	0.0058(18)	0.0023(35)	0.0001(26)	0.0008(20)
C3	0.0207(47)	0.0085(24)	0.0022(12)	−0.0041(28)	0.0022(19)	−0.0006(14)
C4	0.0155(44)	0.0219(29)	0.0058(17)	0.0042(30)	−0.0003(22)	−0.0035(18)
C5	0.0202(49)	0.0093(26)	0.0076(19)	−0.0077(32)	−0.0017(26)	−0.0006(18)
C6	0.0259(66)	0.0184(45)	0.0089(25)	0.0041(45)	−0.0033(35)	−0.0101(29)
C7	0.0378(93)	0.0097(28)	0.0078(23)	0.0057(43)	0.0044(38)	−0.0013(22)
C8	0.0609(99)	0.0190(46)	0.0037(20)	0.0186(70)	0.0032(44)	−0.0045(24)
C9	0.0186(56)	0.0159(39)	0.0059(18)	0.0016(38)	−0.0011(27)	−0.0018(22)
C10	0.0332(84)	0.0211(52)	0.0070(23)	0.0137(56)	−0.0011(38)	−0.0039(29)
O1	0.0342(49)	0.0241(32)	0.0035(10)	0.0096(31)	0.0023(19)	0.0032(14)
O2	0.0219(41)	0.0257(38)	0.0137(23)	−0.0061(34)	−0.0057(25)	−0.0012(23)
O3	0.0174(27)	0.0082(15)	0.0058(10)	−0.0003(17)	−0.0000(13)	0.0012(10)

[a] The anisotropic temperature factors are of the form $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$

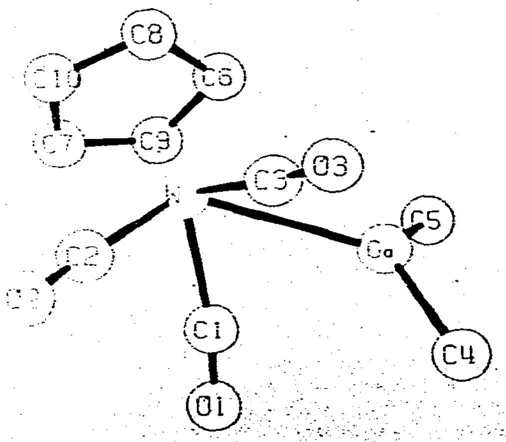

Fig. 1. Molecular structure and labeling of π-$C_5H_5(CO)_3WGa(CH_3)_2$.

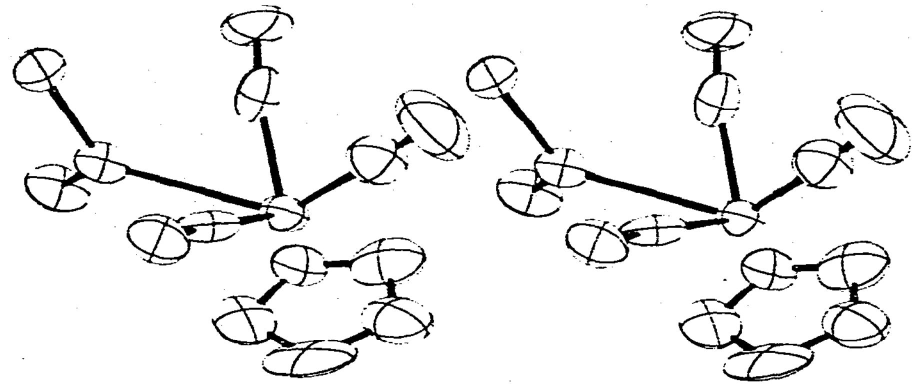

Fig. 2. Stereoscopic view of π-$C_5H_5(CO)_3WGa(CH_3)_2$.

The molecule consists of a tungsten atom bonded to three carbonyls, to a dimethylgallium moiety and to a π-bonded cyclopentadienyl group. The cyclopentadienyl group is centered above the tungsten atom at a distance of 2.00 Å to the center of the ring and 2.35 Å (av.) to the carbon atoms. The W—carbonyl distances average 1.96 Å and the W—Ga distance is 2.71 Å. The carbonyl groups are approximately linear with average W—C—O angles of 175°. These parameters are very similar to those observed in $[\pi$-$C_5H_5(CO)_3W]_3Ga$ [5] and are comparable to those observed in other derivatives of this transition metal moiety.

The orientation of the Ga and three carbonyl groups about the tungsten atom may be approximately described as follows. The gallium atom is opposite C2 with a Ga—W—C2 angle of 124°. The remaining carbonyls Cl and C3 are located

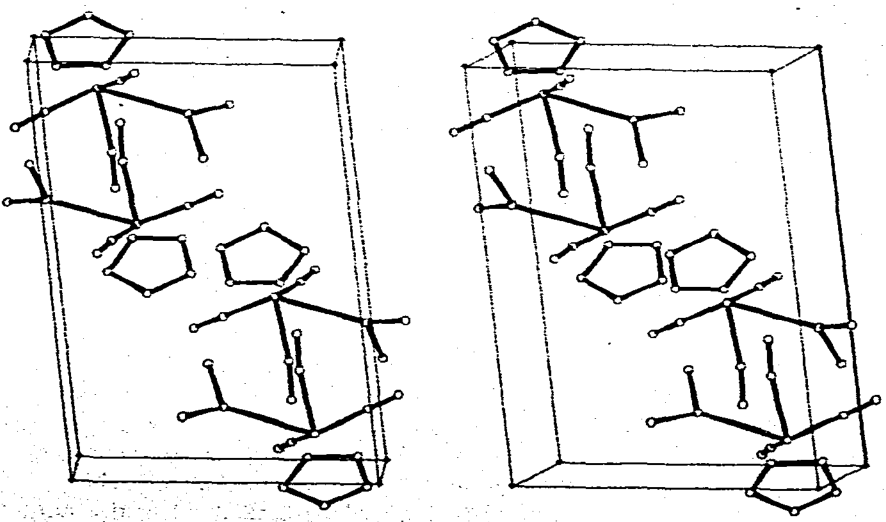

Fig. 3. Stereoscopic packing diagram of π-$C_5H_5(CO)_3WGa(CH_3)_2$.

TABLE 2

DISTANCES AND ANGLES IN π-$C_5H_5(CO)_3WGa(CH_3)_2$

	Distances		Angles
W—C1	2.00(3)	Ga—W—C1	62.0(7)
W—C2	1.98(3)	Ga—W—C2	123.5(7)
W—C3	1.90(2)	Ga—W—C3	67.1(6)
W—Ga	2.708(3)	C1—W—C2	83.1(9)
W—C6	2.35(2)	C2—W—C3	79.7(9)
W—C7	2.35(2)	C1—W—C3	101.8(8)
W—C8	2.34(2)	W—Ga—C5	118.5(7)
W—C9	2.34(3)	W—Ga—C5	115.7(8)
W—C10	2.35(2)	C4—Ga—C5	123(1)
Ga—C4	1.96(2)	W—C1—O1	172(2)
Ga—C5	2.01(2)	W—C2—O2	176(2)
C1—O1	1.14(3)	W—C3—O3	176(2)
C2—O2	1.18(3)	C8—C6—C9	104(3)
C3—O3	1.21(2)	C6—C9—C7	110(3)
C6—C9	1.40(4)	C9—C7—C10	111(3)
C6—C8	1.57(5)	C7—C10—C8	106(4)
C7—C9	1.45(4)	C10—C8—C6	109(3)
C7—C10	1.43(4)		
C8—C10	1.42(5)		
Shortest intermolecular contacts			
O1—O3	3.21		
O1—C10	3.53		
O2—C4	3.45		

symmetrically vis a vis the plane containing Ga, W and C2 and on the Ga side of the plane bisecting the Ga—W—C2 angle.

If we consider the cyclopentadienyl group to occupy three coordination sites, the coordination sphere about the tungsten may be viewed as a 4-3 type structure in which the plane of the Ga and three carbonyl atoms is approximately parallel (dihedral angle = 3°) to the plane of the cyclopentadienyl group.

If we examine the coordination around the gallium atom we find all angles near 120° with the gallium only 0.16 Å removed from the plane defined by W and the two methyl carbon atoms. There is no evidence for Ga—carbonyl oxygen intermolecular association. Similar coordination was observed for $[\pi$-$C_5H_5(CO)_3$-$W]_3Ga$ [5] and it also was noted for the structure of the $In(Co(CO)_4]_3$ species.

Examination of the Ga—C bond lengths (1.96(2) and 2.01(2) Å) and of the C—Ga—C angle (123(1)°) suggests that this species is behaving in a normal manner since these values compare favorably with the corresponding values in triphenylgallium, 1.96 Å and ~120° [32].

NMR Studies on the redistribution reactions of Group II—transition metal derivatives

Reactions, as originally described by Carey and Noltes [32] between transition metal hydrides and Group II organometallics of Zn and Cd were carried out at differing reactant mole ratios to favor production of mixed organometallic species (RMTm, M—Zn, Cd). Diethylzinc and a metal hydride produced ethane and the bis transition metal derivative (Tm_2Zn). Similarly, dimethylcadmium and transition metal hydrides produced methane and the bis(transition metal)-cadmium derivatives as described in the experimental section. The isolation of a mixed organometallic product was not possible. In an attempt to observe the mixed organometallic derivative, a series of studies was carried out in NMR tubes as described. These studies show that spectra recorded early in the reaction period exhibited two singlets in the (C_5H_5) region and a high field hydride resonance characteristic of a transition metal hydride. During the course of the reaction the lines associated with the transition metal hydride decreased in intensity and eventually disappeared. The C_5H_5 resonance lines of the product increased in intensity and shifted downfield as the reaction progressed. In the presence of excess hydride the final product C_5H_5 resonance position was independent of concentration—always identical to the C_5H_5 resonance position of Tm_2Zn prepared and measured independently ($\delta(C_5H_5)[\pi\text{-}C_5H_5(CO)_3Mo]_2Zn = 4.78$; $\delta(C_5H_5)$ $[\pi\text{-}C_5H_5(CO)_3W]_2Zn = 4.97$ ppm). In the presence of excess diphenylzinc, the final position of the C_5H_5 resonance line was variable and upfield of the C_5H_5 resonances for the pure Tm_2Zn derivative.

In separate experiments involving molybdenum hydride and diphenylzinc it was established that the final equilibrium position of the product C_5H_5 resonance was a function of the concentration of unreacted diphenylzinc. Fig. 4 shows a graphical representation of this dependence with the data given in Table 3. We

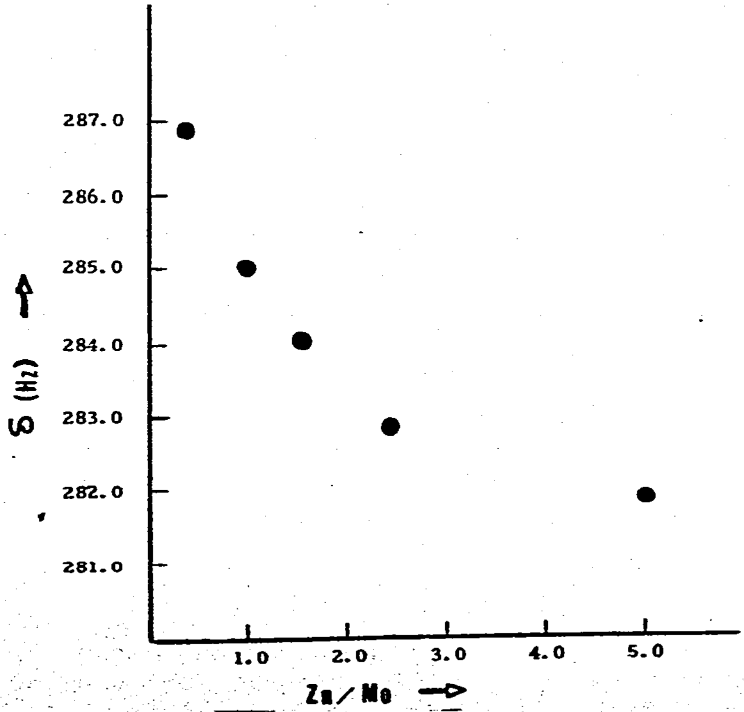

Fig. 4. The chemical shift in Hz of the C_5H_5 resonance of $\pi\text{-}C_5H_5(CO)_3Mo$ moiety as a function of the ratio of Ph_2Zn: $\pi\text{-}C_5H_5(CO)_3MoH$ following reaction (60 MHz, toluene solvent, 35°C).

TABLE 3

CONCENTRATION DEPENDENCE OF PRODUCT C_5H_5 RESONANCE AT EQUILIBRIUM AS A FUNCTION OF $Ph_2Zn : C_5H_5(CO)_3MoH$ MOLE RATIO

$[Ph_2Zn]$ [a]	$[C_5H_5(CO)_3MoH]$ [a]	$Ph_2Zn : C_5H_5(CO)_3MoH$ Mole Ratio	$\delta(C_5H_5)$ [b]	K [c]
0.1060	0.2650	0.40	4.78(2)	
0.1855	0.1855	1.00	4.74(9)	2.4(2)
0.2319	0.1418	1.64	4.73(4)	2.3(7)
0.2650	0.1060	2.50	4.71(6)	1.9(0)
0.3092	0.0618	5.00	4.69(8)	2.1(3)

[a] Units of mols/l in toluene. [b] $\delta(C_5H_5)$ data reported in ppm relative to TMS measured at 60 MHz and 35°C. [c] The equilibrium constants given by $K = \frac{[Ph_2Zn][Tm_2Zn]}{[TmZnPh]^2}$ were determined from the NMR spectra making use of the relationship $\delta_{obs} = N_AS_A + N_BS_B$ to determine the concentrations of Tm_2Zn and TmZnPh.

have demonstrated that at sufficiently large concentrations of diphenylzinc the product C_5H_5 resonance attains a constant value, and that this limiting value ($\delta(C_5H_5) = 4.646$ ppm) can be obtained by mixing diphenylzinc and the bis derivatives (Tm_2Zn) together in appropriate ratios. Analogous experiments with diphenylcadmium and TmH were attempted, but due to the limited solubility of the Tm_2Cd the C_5H_5 resonance signals were not observable under the conditions employed.

These observations are consistent with an initial reaction as given by eq. 2, which produces the unsymmetrical product. This may then undergo a symmetrization as indicated in eq. 3 or react further with TmH. An identical process has been demonstrated for mixed mercury derivatives [10,11].

$$TmH + R_2Zn \rightarrow RZnTm + RH \qquad (2)$$

$$2\ RZnTm \rightleftharpoons Tm_2Zn + R_2Zn \qquad (3)$$

So far it has proven impossible to separate the unsymmetrical phenylzinc derivative and thus it appears to be stable only under the equilibrium conditions of eq. 3 in toluene solutions. The limited studies on the cadmium species suggest that it behaves in a similar manner. However, the insolubility of bis transition metal product is an additional driving force for symmetrization.

Studies on the synthesis and redistribution reactions of gallium—transition metal derivatives

The reaction between π-$C_5H_5(CO)_3MH$ (M = Mo, W) and $(CH_3)_3Ga$ is described stoichiometrically by eq. 4.

$$\pi\text{-}C_5H_5(CO)_3MH + (CH_3)_3Ga \rightarrow \pi\text{-}C_5H_5(CO)_3MGa(CH_3)_2 + CH_4 \qquad (4)$$

There was no evidence for reaction at 40°C, however at 90°C the original pale yellow solution deepened in color over a 3—4 h period. On cooling the solution to 0°C for 24 h, pale yellow crystals of π-$C_5H_5(CO)_3MoGa(CH_3)_2$ formed which were separated by filtration. They are very soluble in aromatic and etheral solvents, slightly soluble in saturated hydrocarbons, and are very sensitive to air oxidation and to moisture. The tris transition metal derivative, Tm_3Ga, was formed in the same way but required increasing the ratio of TmH to $(CH_3)_3Ga$, the reaction temperature to 120°C, and extending the reaction time to five days, when dark orange crystals formed on cooling the solution. The isolated $(\pi\text{-}C_5H_5(CO)_3Mo)_3Ga$ is air sensitive and exhibits similar solubilities to the mixed complexes. The analogous reaction with the tungsten hydride appeared to follow a similar course but no crystalline products formed, even after two weeks. NMR and IR assignments for all compounds are given in Table 4.

In order to further characterize the reaction several samples were prepared in NMR tubes and monitored as a function of reaction time. Prior to heating, the reactants exhibited the single C_5H_5 resonance of TmH, a high field metal hydride resonance, and a singlet assigned to trimethylgallium. During the course of the reaction the signals associated with $\pi\text{-}C_5H_5(CO)_3MH$ decreased in intensity and disappeared after 3—4 h. The resonance associated with $(CH_3)_3Ga$ shifted downfield and broadened as the reaction progressed. In the early stages of reaction, only one NMR resonance in the C_5H_5 region was observed. As the reaction progressed, a second, downfield C_5H_5 resonance appeared along with an upfield singlet (0.9 ppm). The final NMR spectrum, taken prior to cooling and isolation of product, showed two C_5H_5 resonance signals of approximately equal intensity, a singlet at 0.9 ppm, a broad singlet at 0.25 ppm, and a methane signal. These results indicate that multiple products are involved in the reaction.

The NMR spectrum taken of a toluene solution of the initial crystalline product is shown in Fig. 5a and the assignments are given in Table 4. Except for small shifts due to solvent effects and a singlet due to methane, the spectrum of the isolated product and the final reaction spectrum, described above, are identical.

The broad upfield line is indicative of exchanging species. To test this postulate, variable temperature NMR data were obtained. With increasing temperature; the broad, upfield line narrowed to a sharp singlet around 60°C. Upon lowering the temperature, the broad resonance disappeared into the base line at —10°C and two new narrow lines were observed at —60°C. The high field singlet (—0.21 ppm) corresponds to the chemical shift of $(CH_3)_3Ga$ in toluene. The other singlet

TABLE 4

NMR AND IR ASSIGNMENTS FOR MOLYBDENUM AND TUNGSTEN DERIVATIVES OF GALLIUM

Compound	IR cm^{-1} [a]	δ(ppm) [b]
$[\pi\text{-}C_5H_5(CO)_3Mo]_3Ga$	1889w, 1905s, 1964s	5.11 (C_5H_5)
$[\pi\text{-}C_5H_5(CO)_3Mo]_2GaCH_3$	1886s, 1976s	4.87 (C_5H_5) 0.91 (CH_3)
$[\pi\text{-}C_5H_5(CO)_3Mo]Ga(CH_3)_2$	1863s, 1906s, 1987s	4.68 (C_5H_5) 0.38 (CH_3) [c]
$[\pi\text{-}C_5H_5(CO)_3W]_2GaCH_3$	1880s, 1972s	4.87 (C_5H_5) 0.95 (CH_3)
$[\pi\text{-}C_5H_5(CO)_3W]Ga(CH_3)_2$	1860s, 1900s, 1985s	4.66 (C_5H_5)

[a] The IR spectra were obtained on toluene solutions using sealed KBr cells with a pathlength of 0.25 mm. The spectra were calibrated via the 1604.1 cm^{-1} band in polystyrene and recorded on a Perkin—Elmer Model 267 spectrometer. [b] NMR parameters are given in ppm references to internal TMS for toluene solutions. Data were collected on a Varian A60A. [c] Assigned at a probe temperature of —60°C.

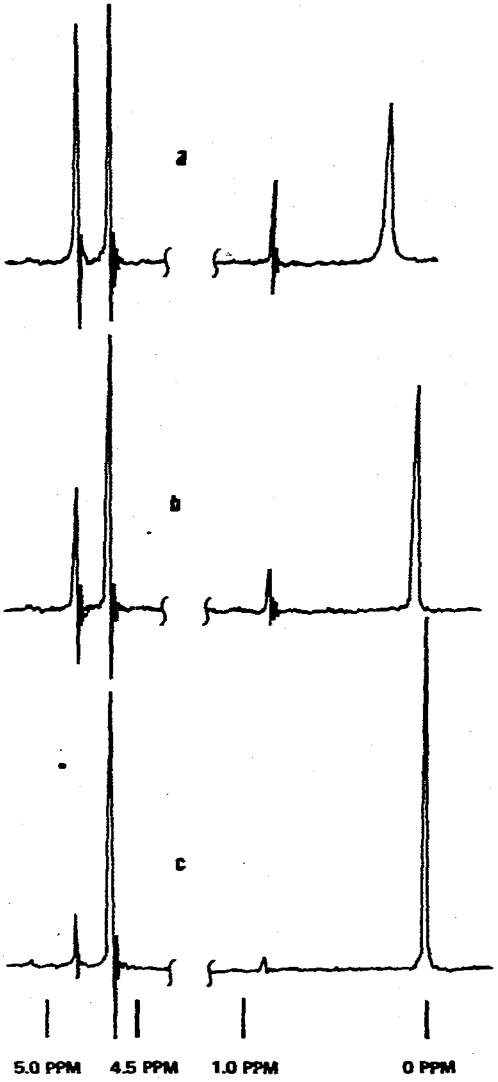

Fig. 5. The NMR spectra of $TmGa(CH_3)_2$ and mixtures of $TmGa(CH_3)_2$ with $(CH_3)_3Ga$. (a) $TmGa(CH_3)_2$; (b) $TmGa(CH_3)_2$: $(CH_3)_3Ga$, 1: ~0.2; (c) $TmGa(CH_3)_2$: $(CH_3)_3Ga$, 1: ~0.5. (Tm = π-$C_5H_5(CO)_3Mo$, 60 MHz, toluene solvent, 35°C.)

centered at 0.38 ppm has an intensity ratio of 6 : 5 relative to the high field C_5H_5 resonance indicating formation of $TmGa(CH_3)_2$.

The two C_5H_5 resonances and the lowfield methyl resonance line were invariant with temperature. These observations establish that (*a*) rapid exchange occurs at room temperature between $(CH_3)_3Ga$ and a new species formed in the reaction, (*b*) a second methyl derivative formed does not undergo rapid methyl exchange with $(CH_3)_3Ga$ under these conditions, and (*c*) two new species con-

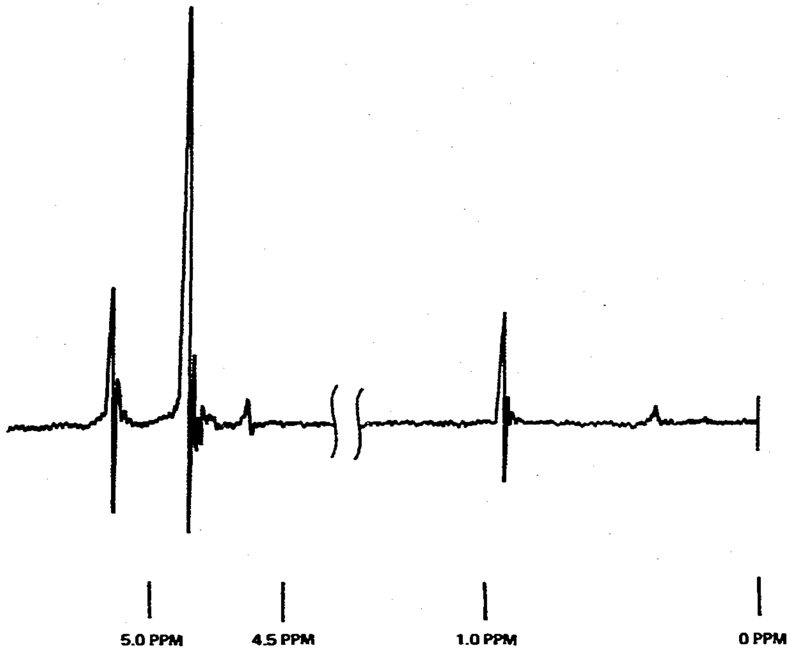

Fig. 6. The NMR spectrum of a sample of $TmGa(CH_3)_2$ following heating in a dynamic vacuum (toluene solution). Assignments from left to right are Tm_3Ga, $\underline{Tm_2}GaCH_3$, $\underline{Tm}Ga(CH_3)_2$, $Tm_2Ga\underline{CH_3}$, and $TmGa(\underline{CH_3})_2$. ($Tm = \pi$-$C_5H_5(CO)_3Mo$, 60 MHz, toluene solvent, 35°C.)

taining C_5H_5 groups are present in solution which do not exchange C_5H_5 groups on the NMR time scale.

To further elucidate these findings increments of $(CH_3)_3Ga$ were added to a toluene solution of the product, $TmGa(CH_3)_2$, with the results shown in Fig. 5b and c. The highfield CH_3 resonance increases in intensity and moves further upfield with addition of $(CH_3)_3Ga$. At the same time the highfield C_5H_5 resonance increases in intensity and the lowfield CH_3 and C_5H_5 resonances both decrease in intensity at the same rate maintaining a 10 : 3 ratio of intensities. These findings support the assignment of the upfield C_5H_5 resonance to $TmGa(CH_3)_2$ with exchangeable CH_3 groups and that of the lowfield C_5H_5 and CH_3 groups to the Tm_2GaCH_3. Further these results establish that the methyl group on Tm_2GaCH_3 does not undergo rapid exchange with the $TmGa(CH_3)_2$ species or with the $(CH_3)_3Ga$ present in solution but reaction does occur at a slower rate permitting conversion of Tm_2GaCH_3 to $TmGa(CH_3)_2$.

Similar experiments, utilizing IR spectroscopy to monitor changes in the ν(CO) region as a function of excess $(CH_3)_3Ga$, were conducted. A solution of π-$C_5H_5(CO)_3MoGa(CH_3)_2$ exhibits five carbonyl absorptions at 1886, 1863, 1906, 1976 and 1987 cm^{-1}. Addition of $(CH_3)_3Ga$ to this solution causes the bands at 1863, 1901, and 1987 cm^{-1} to increase in intensity relative to those at 1886 and 1976 cm^{-1}. These results and the parallel NMR studies permit assignments of the IR bands to be made as indicated in Table 4 and provide support for the equilibrium reactions involving the mixed transition metal alkylgallium derivatives.

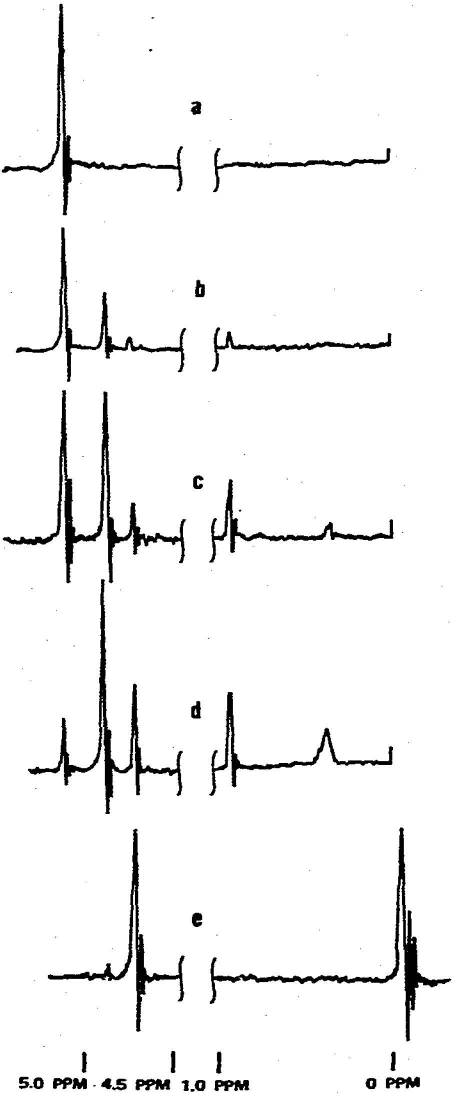

Fig. 7. The NMR spectra of (a) Tm_3Ga and of (b—e) showing the effect of addition of $(CH_3)_3Ga$ to Tm_3Ga. The ratio for Tm_3Ga: $(CH_3)_3Ga$ are approximately (b) 1: ~0.15, (c) 1: ~0.4, (d) 1: ~0.7, and (e) 1: ~3. (Tm = π-$C_5H_5(CO)_6Mo$, 60 MHz, toluene solvent, 35°C.)

To complete the investigation of the processes involved, additional studies were performed. In the first of these, a sample of $TmGa(CH_3)_2$ was heated to 50°C under a dynamic vacuum for a few minutes and underwent a color change from the original pale yellow to a bright yellow-orange. The resulting product was dissolved in toluene and the NMR spectrum shown in Fig. 6 was obtained. Three C_5H_5 resonances corresponding to the Tm_3Ga, Tm_2GaCH_3, and $TmGa(CH_3)_2$ are clearly visible while a large methyl resonance for Tm_2GaCH_3 and a very small resonance for $TmGa(CH_3)_2$ are seen. This indicates that $(CH_3)_3Ga$ can be removed from the system relatively easily yielding the products rich in the transition metal moieties.

The final experiment consisted of addition of $(CH_3)_3Ga$ to a sample of Tm_3Ga obtained as described in the experimental section and monitoring the NMR spectra of these solutions. The results are shown in Fig. 7 and further establish the processes already indicated.

All of the processes can be clearly summarized in eqs. 5—7. Eq. 5 shows the first equilibrium reaction which occurs yielding the mixed transition metal alkyl

$$Tm_3Ga + (CH_3)_3Ga \rightleftharpoons Tm_2GaCH_3 + TmGa(CH_3)_2 \tag{5}$$

$$2\ TmGa(CH_3)_2 \rightleftharpoons Tm_2GaCH_3 + (CH_3)_3Ga \tag{6}$$

$$TmGa(CH_3)(CH_3)^* + (CH_3)_3Ga \rightleftharpoons TmGa(CH_3)_2 + (CH_3)_2Ga(CH_3)^* \tag{7}$$

gallium derivatives.

Eq. 6 represents a disproportionation process established on solution of $TmGa(CH_3)_2$. Equilibrium constants for the process indicated in eq. 6 were established from the integrated intensities of the C_5H_5 resonance lines at room temperature and are estimated for the molybdenum and tungsten derivatives to be 0.13 and 0.19 respectively.

Eq. 7 indicates rapid methyl exchange between $(CH_3)_3Ga$ and the CH_3 groups on $TmGa(CH_3)_2$. All other processes are shown to be slow on the NMR time scale at room temperature as a result of their sharp resonance lines. These slower equilibrium reactions include all exchanges involving transition metal to gallium bond ruptures and the exchange of the methyl group on Tm_2GaCH_3 with either $(CH_3)_3Ga$ or $TmGa(CH_3)_2$. This clearly shows that substitution of an alkyl group by a transition metal moiety on gallium reduces the rate of exchange of groups attached to gallium. The differential rate of transfer of CH_3 groups relative to Tm groups implies that the transition metal—gallium bond is kinetically more stable than the gallium—carbon bond. Further studies are now in progress on these systems in an effort to determine more precisely the factors involved.

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